&Scientific Research University of Baghdad College of Science



Environmental Impact Assessment Of Kirkuk Oil Refinery

A thesis Submitted to the College of Science University of Baghdad in Partial Fulfillment of the Requirements for the Degree of Ph.D., of Philosophy in Geology (Petrology and Mineralogy)

By

Lamyaa Abdul Ameer Ali

M.Sc. Geochemistry

1995

Supervised by

Prof.Dr. Muataz Al-Dabbas

Dr. Adnan H. Afaj

1434

2013

مسم الله الرحمن الرحيم

إِنَّا كُلَّ شَيْءٍ خَلَقْنَاهُ بِقَدَرٍ ﴾

حدق الله العظيم

الايه ٤٩ – سورة القمر

Dedication

To my parent spirits

To my family

To my friends

To all people who helped me

To my country

With Jove

Lamyaa

AKNOWLEGEMENTS

Praise is to Allah and blessings are on the Messenger Muhammad, peace is upon him and his family and his companions.

After approaching from the end of a thousand miles journey I want to express my sincere thanks and gratitude to Dr. Muataz Al-Dabbas and Dr. Adnan H. Afaj to their supervise, guidance, scientific evaluate for the thesis through the duration of the search. I also extend my thanks and gratitude to the President of the Department of geology and to all of my distinguished teachers in the Department of what they gave me of the science and knowledge.

And I have to extend my sincere thanks to the Department of the Environment and Water Research / Ministry of Science and Technology, represented by Mr. Director-General and all the workers at this department to their valuable assistants through the preparation period of this research . I also extend my thanks and gratitude to Dr. Maitham Abdullah Sultan to his help and guidance.

I also thank the workersat the Center of Environmental Research / Soil and Water analysis laboratory for their help to complete the search. I thanked Mr. Issam Abdul- Raheem , Mr.Naseer Abdul-Jabbar, Mr. Bassim Mohammed Hashim , Mr. Bassim Abdul-Sattar, Mr. Issam Abdul-Rahman , Mr. Hasan and Miss Sana Ali for their valuable help and information.

My gratitude to the workers of the North Oil Company especially the environmental department and the safety department for their kindness and helpful at the field works and samples collection, Also I want to thank the workers of Kirkuk oil refinery to their permission of getting samples inside the refinery.

My special thanks to the workers at the department of materials – the Carcinogens Detected Center, Mrs. Iman, Mr. Saad, Mr. Luay Mr. Ammar and Dr. Fadhil Mushin the headmaster of the center.

I also thank my fellow graduate students in the Department of geology. I also thank all those who contributed to the success of this research, even a good word.

The last prayer to thank God.

Lamyaa

Supervisors Certification

We certify that this thesis (**Environmental Impact Assessment of Kirkuk Oil Refinery**) had been prepared under our supervision, in the department of Geology College of Science – University of Baghdad in partial fulfillment of the requirements for the degree of doctor of philosophy in geology.

Signature:	Signature:
Name: Dr. Moutaz A. Al Dabbas	Name: Dr. Adnan H. Afaj
Title: Professor	Title: Expert's
Address: Department of Geology College of Science – University of Baghdad.	Address : Environmental Research Centre - Ministry of Science and Technology

Approved by the Head of Department of Geology

According to the recommendation submitted by supervisors, I forward this thesis for discussion.

Signature:

Name: Dr. Ahmed Sh. Al- Banna

Title: Professor

Address: Department of Geology College of Science – University of Baghdad.

Declaration

This is to certify that the dissertation / thesis titled:

Environmental Impact Assessment of Kirkuk Oil Refinery

Submitted by: Lamyaa Abdul Ameer Ali

Department: Geology

College: College of Science

Has been written my linguistic supervision its language, in its present form, is quite acceptable.

Name:

Address:

Signature:

Confirmation of Examining Committee

We certify that we have read this thesis and as examining committee examined the student in its content and that in our opinion it is adequate with standing as a thesis for the degree of doctor of philosophy in geology (Environmental Impact Assessment of Kirkuk Oil Refinery).

Signature:

Name : Mazen Y. Tamar-Agha

Title: Prof. Dr.

Date : / / 2013

Chairman

Signature:	Signature:
Name : Balsam S. Al-Tawash	Name : Sattar J. Al- Khafaji
Title: Ass.Prof. Dr.	Title: Ass.Prof. Dr.
Date : / / 2013	Date : / / 2013
Member	Member
Signature:	Signature:
Name : Ahmed K. AL-Jumaili	Name : Soran N. Sadeq
Title: Ass.Prof. Dr.	Title: Ass.Prof. Dr.
Date : / / 2013	Date : / / 2013
Member	Member

Signature:	Signature:
Name : Moutaz A. Al Dabbas	Name : Adnan H. Afaj
Title: Prof. Dr.	Title : Expert's Dr.
Date : / / 2013	Date : / / 2013
Supervisor	Supervisor

Approved by the Council of the College of Science

Signature:

Name:

Title:

Abstract

Air, soil and plants are contaminated by polycyclic aromatic hydrocarbons (PAHs) and some heavy metals. In this research environmental samples were taken from 16 sites inside and outside Kirkuk oil refinery to 1.Assess the air, soil and plants contamination due to the Kirkuk refinery systems. 2. Draw detailed air, soil and plants maps to set standards for safe environment. 3. Suggest reliable predictive models to anticipate and manage pollutants concentration in air, soil & plants and their estimate risk of contaminants.

The concentration averages of total suspended particles (TSP) recorded in this study are significantly higher than the permissible allowable limits of the determinants of the Iraqi National standards and the worlds international allowable limits for both periods of this study : October 2010 and March 2011.

Comparing the results obtained, it is found that the averages of CO are lower than what is allowed in the national and international worldwide limits for both periods October 2010 and March 2011. All the maximum values are recorded at locations far from the refinery. The carbon dioxide concentrations are all higher than those allowed in the

national and international world limits and for all the periods and at all sites of the studied area. The results of NO₂ at the studied area show that the average values are slightly higher than the allowable national and international limits for both periods. The concentration of SO₂ in the air in October 2010 was slightly higher than what is permitted and allowed in the worlds standard limitations and they were lower than the national limitation. During March 2011, no record of any concentration of SO₂ was made except of one site (0.1ppm).

The concentration of Lead in the air of the studied area in October was higher than the limits, whereas this concentration in March recorded lower values than the national and world limits,. The concentration of Copper in air during the two periods were lower than what the worlds allowable standard. It was found that Nickel concentrations were higher than the worlds allowable standard limitaions. Chromium concentrations were also investigated in this study and it was found that the average of Chromium in the air of the studied area was different from the two averages. It proves that there is no effect of seasonal changes on the concentration of this element.

The high concentration of PAHs in air of the studied area in October as a total was $67.685 \mu g/m^3$ meanwhile the high concentration in March was rather high (7924.27 $\mu g/m^3$). This increment in PAHs concentrations at this period can be referred to the increasing fuel combustion operations at the location such as the operations of the power plant which functions increasingly during the winter months.

The concentrations of Pb, Cu and Ni in the soil of the studied area compared with the world average were lower during the two periods of measurements. Chromium concentrations in soils have increased during March. While recovered Cadmium was higher than the world allowable average.

The average of total concentrations of PAHs in the soil of the studied area in March was (10.92ppb) which was lower than their values during October (26.92ppb). This is a result of the meteorological conditions present such as temperature, rainfall and prevailing wind.

The average of Lead, Copper, Chromium and Cadmium in leaves of Eucalyptus of the studied area decrease from October to March due to the effect of meteorological elements of the different seasons. Nickel concentrations found on Eucalyptus leaves taken from the study area increased between the two periods due to the fuel combustion operations of the refinery and the oil fields near the studied area. The average of total concentrations of PAHs extracted from Eucalyptus leaves on March was (67.41ppb) which was higher than their values during October (40.34ppb). This is due to air temperatures decrease during the fall and winter seasons; evergreen plants scavenge the majority of emitted PAHs.

The GIS modeling is applied in this study on the results of chemical analysis of different environmental elements (air, soil and plants) to represent the distribution of the studied pollutants in the environment and determinate the most affected areas by these pollutants.

Table of Contents

Subject	Page
Acknowledgements	i
Abstract	ii
Table of Contents	
List of Tables	
List of Figures	
List of Abbreviations	
Chapter One: Introduction	
1.1 Preface	1

1.2	Literature Review	3
1.3	Aim of the study	7
1.4	The Study Area	8
1.4.1	The location	8
1.4.2	General geology of the study area	9
1.4.3	Hydrogeology of the study area	11
Chapter Two	: Meteorology	0
2.	The climate of the study area	12
2.1	Temperature	12
2.2	Rainfall	15
2.3	Relative Humidity	16
2.4	Wind Speed and Direction	17
Chapter Thre	e : Methods and Materials	0
3.	Introduction	19
3.1	Field works	20
3.1.1	Field Sampling Devices	22
3.1.2	Preparation of air samples	29
3.1.3	Preparation of soil and plant samples	31
3.2.	Laboratory works	33
3.2.1.	Digestion method of air filters samples	33
3.2.2.	Digestion method of soil samples	34
3.2.3.	Digestion method of plant samples	35
3.2.4.	Lab Devices	36

3.2.5.	Chemicals used	40
3.2.6.	Extraction method of PAH's from air filters	41
3.2.7.	Extraction methods of PAH's from soil and plant samples	42
3.3.	Precision and Accuracy	46
3.4.	Data Analysis and Fitting Model	48
Chapter Four	: The Results and Discussion	
4.	Introduction	48
4.1	Air pollution	48
4.1.1	Total Suspended Particles	49
4.1.2	Gasses	55
4.1.2.1	Carbon Monoxide (CO)	55
4.1.2.2	Carbon Dioxide (CO ₂)	56
4.1.2.3	Nitrogen Dioxide (NO ₂)	57
4.1.2.4	Sulfur Dioxide (SO ₂)	57
4.1.3	Heavy metals	63
4.1.3.1.	Lead (Pb)	65
4.1.3.2	Copper (Cu)	65
4.1.3.3	Nickel (Ni)	65
4.1.3.4	Chromium (Cr)	66
4.1.3.5	Cademium (Cd)	66
4.1.4	Polycyclic aromatic hydrocarbons	74
4.2	Soil pollution	89

4.2.1	Heavy metals	89
4.2.1.1	Lead (Pb)	90
4.2.1.2	Cupper (Cu)	91
4.2.1.3	Nickel (Ni)	91
4.2.1.4	Chromium (Cr)	92
4.2.1.5	Cadmium (Cd)	92
4.2.2	Polycyclic aromatic hydrocarbons	101
4.3	Plant pollution	114
4.3.1	Heavy metals	115
4.3.1.1	Lead (Pb)	115
4.3.1.2	Copper (Cu)	116
4.3.1.3	Nickel (Ni)	117
4.3.1.4	Chromium (Cr)	117
4.3.1.5	Cadmium (Cd)	118
4.3.2	Polycyclic aromatic hydrocarbons	126
Chapter Five	: Modeling	
5.1	Introduction	142
5.1.1	Geographic Information Systems (GIS) Applications	144
	1. IDW (ArcGIS 10)	146
	2. Reclassification (ArcGIS 10)	147
	3. Cell Statistics	148
5.2	Arc GIS 10 modeling for the pollutants impacts	149

	on the studied area	
5.2.1	Dispersion modeling of heavy metals in air	149
5.2.2	Dispersion modeling of heavy metals in Soil	153
5.2.3	Dispersion modeling of heavy metals in Plant	156
5.2.4	Dispersion modeling of PAHs in air	160
5.2.5	Dispersion modeling of PAHs in Soil	163
5.2.6	Dispersion modeling of PAHs in Plant	167
Chapter Six :	Conclusions and Recommendations	<u></u>
6.1	Conclusions	171
6.1.1	Air pollution	171
6.1.2	Soil pollution	172
6.1.3	Plant Pollution	173
6.2	Recommendations	174
References		<u> </u>
Appendixes		
Appendix (1)	Appendix (1)HPLC & GC-MS Chromatograms of PAHs in the Air of the Studied Area at the Two Periods.	
Appendix (2)	HPLC & GC-MS Chromatograms of PAHs in the Soil of the Studied Area at the Two Periods.	
Appendix (3)	pendix (3) HPLC & GC-MS Chromatograms of PAHs in the Plant of the Studied Area at the Two Periods.	

List of tables

Table	Title	Page
3-1	GPS Coordinates of the sampling sites	22
3-2	A list of the Climate elements that were measurement at the studied area during October 2010.	27
3-3	A list of the Climate elements that were measurement of the studied area during March 2011.	28
3-4	The recovery program of moving phase (Acitonitryle - water) used to detect PAHs in this study	41
3-5	Retention time and concentration of standards mixture for the PAHs detected by HPLC	43
3-6	Retention time and concentration of standards mixture for the PAHs detected by GC-MS.	45
4-1	Local and global standard of some air pollutants (Ministry of Environment - Air Pollution Department for the year 2008.(AL-Saady 2012)	51
4-2	TSP concentrations in the studied area and comparison with values of national and world limits.	53
4-3	Gasses concentrations measurements in the sites of studied area (ppm) in October period 2010	58
4-4	Gasses concentrations measurements in the sites of studied area (ppm) in March period 2011	59
4-5	Global standard of the suspended particles and trace elements	64
4-6	Heavy metals concentrations in the air of the studied area in October 2010	67
4-7	Heavy metals concentrations in the air of studied area in March period 2011	68

4-8	PAHs concentrations in air of the studied area in October 2010	78
4-9	PAHs concentrations in air of the studied area in March 2011	79
4-10	Heavy metals concentration in soil of the studied area in October 2010	93
4-11	Heavy metals concentrations in soil of the studied area in march 2011	94
4-12	Heavy metals averages in soils of some national and world udies (modified after Salman 2007)	95
4-13	PAHs concentrations in soil of the studied area in October 2010	103
4-14	PAHs concentrations in soil of the studied area in March 2011	104
4-15	Heavy metals concentrations in leaves of plants (Eucalyptus) in October 2010	119
4-16	Heavy metals concentrations in leaves of plants (Eucalyptus) in March 2011	120
4-17	PAHs concentrations in plant leaves of the studied area in October 2010	128
4-18	PAHs concentrations in plant leaves of the studied area in March 2011	129

List of figures

Fig.	Title	Page
1-1	The topographic map of Iraq showing the location of Kirkuk governorate	8

1-2	The topographic map of Kirkuk governorate showing the sites of sampling	9
2-1	The annual means of air temperature in Kirkuk for the period from (2002-2010)	13
2-2	The annual means of maximum temperature in Kirkuk for the period from (2002-2010).	14
2-3	The annual means of minimum temperature in Kirkuk for the periods from (2002-2010).	14
2-4	The annual rates of rainfall in Kirkuk for the period from (2002-2010).	16
2-5	The annual rates of relative humidity of Kirkuk for the periods from(2002-2010)	17
2-6	The annual rates of wind speed in Kirkuk for the period from (2002-2010).	18
2-7	The annual rates of wind directions in Kirkuk for the period from (2002-2010) using wind rose program.	18
3-1	GIS Map showing the selected locations of sampling sites at the study area	21
3-2	Mono and dioxide carbon (CO, CO ₂) concentration measuring devise	23
3-3	Image of device used in the measurement of (H_2S, SO_2, NO_2) gases concentrations in the air	24
3-4	Front and back view of Low Air Sampler (Sniffer) devise features	25
3-5	Anemometer devise used for measuring wind speed	25
3-6	Image of the device that was used for the measurements of air temperature and humidity	26
3-7	Air sampling at one of the studied area sites	31

3-8	Soil sampling	32
3-9	Plant sampling of eucalyptus tree	32
3-10	Image for the Atomic Absorption Spectrometer (AAS) devise that was used during this study	36
3-11	HPLC devise.	39
3-12	GC-MS devise	40
3-13	HPLC Chromatogram of standard mixture for 16 EPA priorities PAHs	44
3-14	GC-MS chromatogram of standards mixture of PAHs compounds	46
4-1	Total suspended particles distribution in air of the studied area in October 2010 and March 2011.	54
4-2	GIS map showing CO distribution in air for the studied area for the period of October 2010 and March 2011	60
4-3	GIS Map showing the CO ₂ distribution in air at the studied area in October 2010 and March 2011	61
4-4	GIS Map showing NO ₂ distribution in the air of the studied area in October 2010 and March 2011	62
4-5	GIS map showing Lead (Pb) distribution in air of the studied area in October 2010 and March 2011.	69
4-6	GIS map showing Cupper (Cu) distribution in air of the studied area in October2010 and March2011	70
4-7	GIS Map of Nickel distribution in air of the studied area for the two periods of the study	71
4-8	GIS map showing Chromium distribution in air of the studied area in october 2010 and march 2011	72
4-9	GIS map for Cadmium distribution in air of the studied	73

	area in October 2010 and Marc 2011.	
4-10	Molecular structure of the 16 polycyclic aromatic hydrocarbons (PAHs) selected as priority pollutants by the American Environmental Protection Agency (EPA). (Henner et al 1997)	76
4-11	GIS Map showing PAHs (total) distribution in air of the studied area in october 2010 and march 2011	80
4-12	GIS Map showing Naphthalene distribution in air of the studied area in October 2010 and March 2011	81
4-13	GIS Map showing Acenephthen and Fluorine distribution in air of the studied area in October 2010	82
4-14	GIS Map showing Phenanthren and Anthracene distribution in air of the studied area in October 2010	83
4-15	GIS Map showing Benzo(a)Anthracene distribution in air of the studied area in October 2010 and March 2011	84
4-16	GIS Map showing Benzo (b) fluranthene distribution in air of the studied area in October 2010 and March 2011	85
4-17	GIS Map showing Dib (ah)Anthracene distribution in air of the studied area in October 2010 and March 2011	86
4-18	GIS Map showing Benzo (ghi)perylene distribution in air of the studied area in October 2010	87
4-19	GIS Map showing Fluranthene and Benzo (k) Fluranthene distribution in air of the studied area in March 2011 .	88
4-20	GIS Map showing Lead (Pb) distribution in soil of the studied area in October 2010 and march 2011	96
4-21	GIS Map showing Copper distribution in soil of the studied area in October 2010 and March 2011	97

4-22	GIS Map showing Nickel distribution in soil of the studied area in October 2010 and March 2011	98
4-23	GIS Map showing Chromium distribution in soil of the studied area in October and march 2011	99
4-24	GIS Map showing Cadmium distribution in soil of the studied area in October2010 and March2011	100
4-25	GIS Map showing Total PAHs distribution in the soil of the studied area in October2010 and March2011	105
4-26	GIS Map showing Fluorine distribution in the soil of the studied area in October 2010 and March 2011	106
4-27	GIS Map showing Acenephthene and Phenanthrene distribution in the soil for the studied area in October 2010	107
4-28	GIS Map showing Anthracene distribution in the soil of the studied area in October 2010 and March 2011	108
4-29	GIS Map showing Fluoranthene distribution in the soil of the studied area in October 2010 and March 2011	109
4-30	GIS Map showing Pyrene distribution in the soil of the studied area in October 2010 and March 2011	110
4-31	GIS Map showing Benzo(a)Anthracene and Benzo(k)Fluoranthene distribution in the soil of the studied area in October 2010	111
4-32	GIS Map showing Benzo (a) Pyrene and Benzo (ghi) Perelyne distribution in the soil of the studied area in October 2010	112
4-33	GIS Map showing Naphthaline and Dibenzo(ah)Anthracene distribution in the soil of the studied area in March 2011	113
4-34	Pb distribution in Eucalyptus leaves taken from the	121

	studied area in October2010 and March 2011	
4-35	Cu distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011	122
4-36	Ni distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011	123
4-37	Cr distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011	124
4-38	Cd distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011	125
4-39	GIS Map showing Total PAHs distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011	130
4-40	GIS Map showing Acenephthene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011	131
4-41	GIS Map showing Fluorene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011	132
4-42	GIS Map showing Phenanthrene and Fluoranthene distribution in Eucalyptus leaves of the studied area in October 2010	133
4-43	GIS Map showing Anthracene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011	134
4-44	GIS Map showing Pyrene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011	135
4-45	GIS Map showing Benzo(a)Anthracene and Benzo(ghi)Perelyne distribution in Eucalyptus leaves of the studied area in October 2010	136

4-46	GIS Map showing Dibenzo(ah)Anthracene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011	137
4-47	GIS Map showing Chrysine and Benzo(b)Fluoranthene distribution in Eucalyptus leaves of the studied area in March 2011	138
4-48	GIS Map showing B(a)Pyrene distribution in Eucalyptus leaves of the studied area in March 2011	139
5-1	Arc GIS model for Air pollution (heavy metals) of the studied area in October 2010 and March 2011	148
5-2	Arc GIS model for Air modeling of heavy metals at the studied area	149
5-3	showing the process flow charts of air pollution Arch GIS modeling	150
5-4	Arc GIS model for Soil pollution (heavy metals) of the studied area in October 2010 and March 2011	152
5-5	Arc GIS model for Soil pollution of heavy metals at the studied area	153
5-6	showing the process flow charts of soil pollution Arch GIS modeling	154
5-7	Arc GIS model for Plant pollution (heavy metals) of the studied area in October 2010 and March 2011	155
5-8	Arc GIS model for Plant pollution with heavy metals at the studied area	156
5-9	showing the process flow charts of plants pollution in Arc GIS modeling	157
5-10	Arc GIS model of (PAHs)pollutants in the air of the studied area in October 2010 and March 2011	159

5-11	Arc GIS model of (PAHs) pollutants in the air of the studied area	160
5-12	showing the process flow charts of Air modeling for (PAHs) pollutants of the studied area	161
5-13	Arc GIS model showing Soil pollution with (PAHs) for the studied area in October 2010 and March 2011	163
5-14	Arc GIS model showing Soil pollution with (PAHs) for the studied area	164
5-15	showing the process flow charts of Soil modeling for (PAHs) pollutants of the studied area	165
5-16	Arc GIS model showing Plant pollutants with (PAHs) for the studied area in October2010 and March 2011	167
5-17	Arc GIS model showing Plant pollutants with (PAHs) for the studied area	168
5-18	e process flow charts of Plant pollution with (PAHs) in Arc GIS modeling	169

List of Abbreviations

TSP	Total Suspended Particles
PAHs	Polycyclic Aromatic Hydrocarbons
HPLC	High Performance Liquid Chromatography
GC-MS	Gas Chromatography- Mass
EPA	Environmental Protection Agency
GIS	Geographic Information System
GPS	Global Positioning System

AAS	Atomic Absorption Spectrometer
LSD	Least Significant Difference
NAP	Naphthalene
ACE	Acenaphthene
ACY	Acenaphthylene
FLU	Fluorene
РНЕ	Phenanthrene
FLUA	Fluoranthene
CHR	Chrysene
ANT	Anthracene
B(a)A	Benzo (a) anthracene
B(k)F	Benzo (k) fluoranthene
B(b)F	Benzo (b) Fluoranthene
PYR	Pyrene
DIB(ah)A	Dibenzo (a, h) anthracene
B(a)P	Benzo (a) pyrene
B(ghi)P	Benzo (g, h, i) perylene
IndP	Indeno (1,2,3-cd) Pyrene
IDW	Inverse distance weighted

Chapter One

Introduction

1.1 Preface

The high and rapid growth at the last century causes many different problems, one of them is the environmental pollution that pollute the environmental elements, such as (Air, water and Soil), which begins to make a serious question that needs a rapid solution. The environmental pollution known as the chemical, physical and biological changes in the environment lead to the emergence of situations of a negative and direct impact on it (Al-Qaisy and Al-Shammary 1997).

The environmental pollution problems have increased through the twentieth century due to the technological and industrial development. The environmental pollution have a major development with the evolution of life and become an important science. The growth and development came through the sense of great imbalance happened to the environment, especially those on contact with human beings.

The environmental pollution at the present time is the main concern of the world's (industrialized and developing countries), because it forms a direct threat human health to and other organisms. In order to develop agriculture had to be use chemical fertilizers and different kinds of pesticides to eliminate pests, for the development of industry established mega-projects to provide raw materials and production of various materials to fill a local need, as the increase in population to increase the demand for various industrial materials. The contribution of all these events release loads of pollutants to the environment such as hydrocarbon compounds and other materials, which needs for measurements, specifications and limits to protect of these pollutants in water, air and soil. Some countries and organizations had proceeded to develop legislation and publications to reduce contaminants and limiting the concentrations before arrival to the dangerous levels (Afaj et al 2008).

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, mostly oil industry activities using a 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 their existence inside the limits of the cities, or their existence inside urban area (Afaj et al 2008), such as Kirkuk oil refinery. The oil refinery industry considered as an important source for air pollutants, where volumes of the released pollutants from these industries were estimated to be in millions of tons per year (Afaj et al 2008).

Air pollutants come in the form of gases and finally divided solid or liquid particles. These air pollutants can be classified as primary- and secondary-pollutants, where the primary- pollutants are those emitted directly into the atmosphere by the sources, such as: total suspended particulate (TSP), SO_x , NO_x , HC and CO. The secondary air pollutants are the ones that are formed as a result of reactions between primary pollutants and other elements in the atmosphere, such as ozone (O₃), which is an invisible toxic gas that is the primary ingredient of urban smog. It is well known these air pollutants are very harm to all living being, and especially to human being, where not only the occupationally exposed workers(high- risk population group) but the community at large(low- risk population group) may suffer due to increased air pollutants in the environment(Afaj et al 2008).

The health effect caused by air pollutants may range from subtle biochemical and physiological changes to difficulty breathing, wheezing, coughing and aggravation of existing respiratory and cardiac conditions. These effects can result in increased medication use, increased doctor or emergency room visits, more hospital admissions and even premature death.

In this study the work conducted on analyzing the pollution levels in the air, soil and plants of the area in and around Kirkuk Refinery due to its emissions to the environment. The study applied the Arc view program one of GIS programs.

1.2 Literature Review

Critically analyze relevant and recent literature with a point of view of defining what has been done and what is needed, establishing the need for this study, defining the problem, and establishing the significance and potential contributions of this study.

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. But different works and studies in the field of environmental engineering, geology, chemistry, physics and biology, have been undertaken during the last 15 years. Several studies had been carried out by Iraqi scientists and researchers on environmental pollution in Iraqi governorates especially in some industrial areas, and in other areas, such as:

• Kanbour et al., (1985) carried out a study on the TSP and the concentration of some heavy metals in it. It was found that the main constituents of TSP are from the solid particulate emitted by industrial activities and the other particles such as dust.

- Sufuan, (1990) carried out a theoretical study on the environmental assessment for Baiji electrical power planet. He had suggested a practical solution through applying a theoretical model to estimate, the concentrations of pollutant in urban site locating in the prevailing wind direction, and to find the relations controlling the distribution of these pollutants.
- Al-Tekriti,(1997) investigated the pollution resulted from two power planets (Al-Daura and south Baghdad power planet) throughout determination of the concentrations of polluted gases (HC, CO,SO₂ and NO₂) emitted from these two power planets ,by applying and using Gaussian model to estimate the distribution of the pollutants.
- Al-Qaisy & Al-Shammary, (1997) studied the petroleum pollutants of north company field's central and northern Iraq.
- Al- Rawi, (1997) studied the environmental pollution features and treatment in north oil company.
- Othman et al, (1998a) studied the effect of the industrial gasses whom effluents from the north gas complex on the environmental pollution at the around area.
- Othman et al, (1998b) studied the effect of industrial polluted gasses released from north gas complex on the workers' health.
- Jawad , (1998) studied the Iraqi oil derivatives and their impacts on the environmental pollution .
- Al-Hamdany, (2000) carried out a study on gasses emission from the burner and their effects on environmental pollution.
- Afaj, et al, (2000) studied the air pollutants, such as TSP, HC, CO, NO_X, SO_X and H₂S that emitted to air by Baiji refinery. The

researchers had found that the concentrations of some of these pollutants are higher than the standard values.

- Dawood, (2003) carried out a specific study for the pollution percentage with polycyclic aromatic hydrocarbons in the Iraqi heavy oil shale and for wheat infected with telletia.
- Husain (2003) studied polycyclic aromatic hydrocarbons in Iraqi environmental samples where simple RP-HPLC technique has been tried for the optimization separation of standards poly aromatic hydrocarbons by using Supelcosil LC-PAH column (150.0X4.6 mm I.D).
- Al-Maliki, (2005) investigated the environmental pollution of the soil and air in Baghdad city using GIS and to draw maps of the level of the pollution by the heavy metals.
- Abdel Wahid, (2005) studied the concentration of some atmospheric pollutants (CO, SO₂ and T.S.P.) in Baghdad and how they are affected by the main meteorological parameters (Temperature, pressure, wind speed, relative humidity).
- Al-Samarae, (2006) studied the air pollution, TSP and lead in selected fuel stations in the city of Baghdad. Also he determined Pb concentration in blood from random samples of workers in these fuel stations. He found that 50% of the workers have high concentrations of Pb in comparison with standard values.
- Al Maliky, (2006) studied and determine the effects of air pollution with T S P and some heavy metals on some perennial plants, such as *Ziziphus spina chisti, Nerium oleander and phoenix dactylifera*, in the city of Baghdad.

- Ali, (2007) studied the concentrations of heavy metals in surface soils of the Haweja area western of Kirkuk.
- The research of Sabry (2007) was dealing with Optimizing the conditions for the Separation of the Poly aromatic hydrocarbons (PAHs) using RP-HPLC technique to achieve best resolution in a very short time.
- Salman, (2007) measured the concentrations of heavy metals (Pb, Ni, Co, Cd, Cu, Fe and Cr) in several ecological components, (Soil, surface water, palm fronds ash, dust and molluscan Shells) in Al-Basra Province and indication to the probable sources of pollution and proposing the proper treatment methods as well as comparing the concentrations of heavy metals in the studied ecological components with local and international ranges.
- Afaj, et al (2008) studied the pollutants such as TSP, HC, CO, NO_x, SO_x, H2S and the distribution of these pollutants within the production units of Al-Daura refinery to study the environmental impact of the high concentrations for the pollutants on the workers in the refinery, throughout the determination of some toxic pollutants (Pb) in blood, hair, and fingernail samples for these workers.
- Hashim (2009) measured the air pollutants concentrations such as Total Suspended Particles (TSP), Lead (Pb), Carbon Oxides (CO,CO₂), Sulfur Dioxide (SO₂), Nitrogen Dioxide (NO₂), and Hydrogen Sulfide (H₂S) in Baghdad city
- Mohammed, (2009) studied the pollution caused by the vehicle exhausts and oil trash burning in Kirkuk city.

The studies on poly aromatic hydrocarbons and their environmental effects are very little in Iraq.

1.3. Aim of the study

Investigation for the air, soil and plants of the area around Kirkuk refinery has done to identify the places and the nature of contamination, and the harmful chemical and biological compounds are essential and vital to the Kirkuk environment and people health.

The following steps were achieved:

1. Assess the air, soil and plants contamination due to the Kirkuk refinery systems.

2. Draw detailed air, soil and plants pollutants maps to set environmental standards for safe environment.

3. Suggest reliable predictive models to anticipate and manage pollutants concentration in air, soil and plants and their estimate risk of contaminants.

It should also include measures that conserve and control of domestic air pollution, soil and plants from quality degradation or depletion by assessment of environmental controlling factors.

1.4 The Study Area

1.4.1. The location

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.1-1, 2).

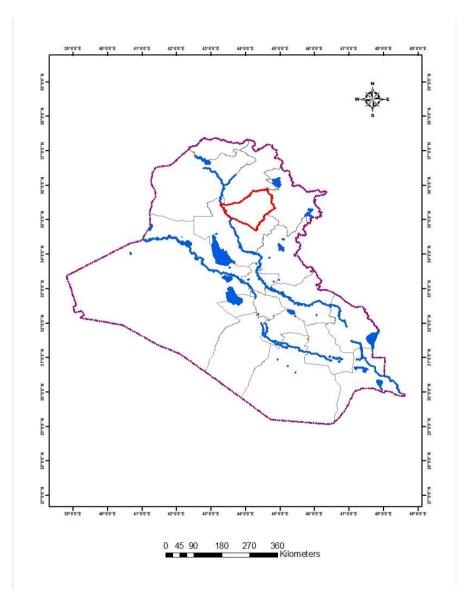


Fig (1-1): The map of Iraq showing the location of Kirkuk governorate.

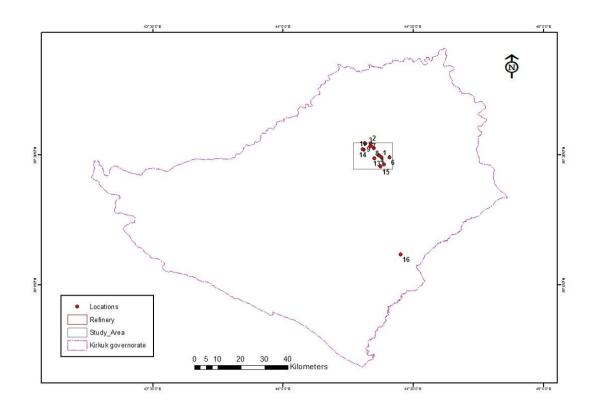


Fig. (1-2): The map of Kirkuk governorate showing the sites of sampling

1.4.2. General geology of the Study Area

Kirkuk Governorate is covered by recent sediments and sedimentary rocks. The geological formations outcrop has a large extension ranging in age from Miocene (Fatha fm.) to Quaternary sediments. The common rocks are limestone and clastics with the presence of gypsum rocks. These formations from the oldest to the recent are as follows: - Fatha formation M. MioceneInjana formation U. MioceneMuqdadiya formation U. Miocene - PlioceneBai Hassan formation PlioceneQuaternary deposits and recent Sediment

Tamim province is divided in terms of two main geomorphological parts. The first part is a flat floor and includes the hills and the undulating land and the study area is located within this region, while the second part contains the mountainous areas and those located in the north and northeast of the province. The province is divided into five geomorphologic units, namely, (structural - erosional) - erosional - river - wind evaporative.

The following units appear in the study area:

1 - Units of Denudation Origin. Include slope deposits - deposits of multiple origins.

2 - Units of Fluvial Origin. Include deposits of flood plains and river terraces.

3 - Units of Evaporation Include Gypcrete deposits.

The Geomorphological processes in the region are weathering and erosion (Sissakan, 1993 in Majeed, 2004).

The study area is located within mountains foothill zone. This range is the central unit in the area of the unstable shelf and has a broad belt between the Iraq - Turkey and the Iraqi-Syrian border in the northwest and western edge of the Iraqi - Iranian in the Diyala River in the south east .The area was affected by the movements in the Alpine Orogeny in the late Triassic. This area is characterized by a thick sedimentary cover and the convex folds of a long and narrows with parallel axes separated by a wide concave folds. (Buday and Jassim, 1987). The presence of deep cracks along the convex or parallel with the folds, which in turn divided the region into secondary belts, namely:

1 - Hamrin – Makhoul Belt (Hamrin-Makhul Subzone)

2 - Chamchamal - Botmah Belt (Chemchemal-Butmah Subzone) (Buday and Jassim, 1987).

Hamrin zone contains the feet of the mountains on a large number of convex folds, including Bai Hassan fold, Kirkuk fold, Jambour fold, Hamrin fold, Makhoul fold, the Dome of the Baba, the Dome of Avanah, the Dome of the Khurmala also contain a large number of faults associated with the existing folds (Sissakan, 1993 in Majeed, 2004). The study area is located within Chamchamal - Botmah Belt.

1.4.3. Hydrogeology of the study area

The region is fed by Al-khassa River that runs through inside the city. The quality of groundwater changes depending on the rock quality. The reservoirs are composed of limestone and clastic rocks. In exposed areas where the configuration, the water-type composition is of sulfate in the Bai Hassan bicarbonate type water. The depth of the groundwater oscillating due to topography and structure of the region. The hydro chemical studies found that the percentage of sulfates high in the study area at Quaternary deposition due to the presence of a high percentage of calcium sulfate (Gypsum) in the region (Majeed, 2004).

Chapter two

Meteorology

2. The climate of the study area

The climate of Iraq is generally continental, with hot and dry summers, and cool rainy winters. In northeast of the country, in the mountains, the climate is continental with dry, hot summers and cold, rainy winters. The temperature, wind speed and rainfall affect the concentration of air pollutants in the atmosphere and therefore changes in climatic and environmental atmosphere. Elements of the atmosphere such as the temperature and relative humidity, wind speed and amount of rainfall play a key role in controlling the spread of various air pollutants (Hashim, 2009).

The study area is located at the northern part of Iraq, when the wind prevail north-western (Iraqi Meteorological Organization, 2011) and follows the climate of the Mediterranean basin. Following is the profile elements of the atmosphere and its role in the spread and impact of pollutants:

2.1 Temperature

The very high temperature during the day and the accompanying heating of the earth's surface lead to movements of air that play active work on the dissemination of pollutants vertically to the greatest extent possible, while the night cooling of the earth surface and the air near it control the air downward movements and stability of air, as generated by the concentration of most air pollutants near the surface of the earth and vertical spread is limited, raising the density of pollutants near the surface of the earth (Mosa, 2000 in: Hashim, 2009).

The temperature rise during the summer season, which starts from May and ends during the first days of October, and reaches higher temperatures during July and August, and decreases during the winter season, which starts from November through the end of March. It reachs lower temperatures during January and February, noting a difference in temperature between the residential area, agricultural, and this is due to the fact that cement and construction materials from paved roads emitting heat and to the effect of plants on the meteorological conditions.

Figures (2-1, 2, 3) represents mean of air temperature, maximum and minimum annual rates of temperature in Kirkuk city for the period from (2002-2008). From these figures we can notice that they are unimodal that reflects the continental effects on the meteorological conditions of the study area.

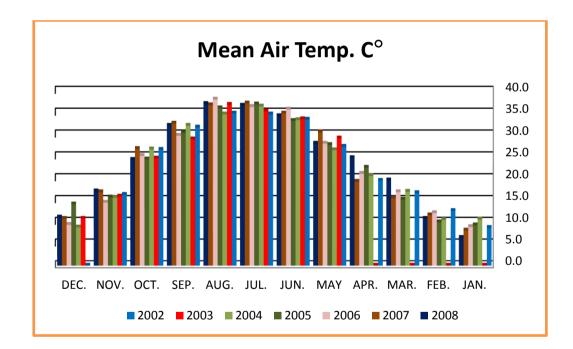


Fig. (2-1): The annual means of air temperature in Kirkuk for the period from (2002-2008)

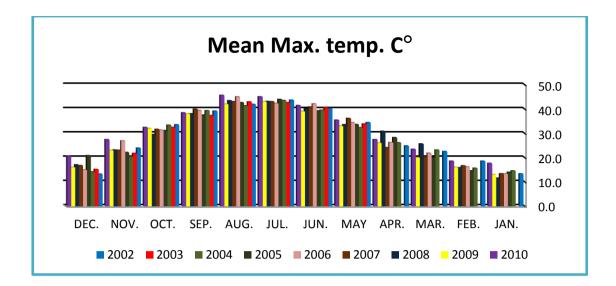


Fig. (2-2): The means annual of maximum temperature at Kirkuk for the period from (2002-2010).

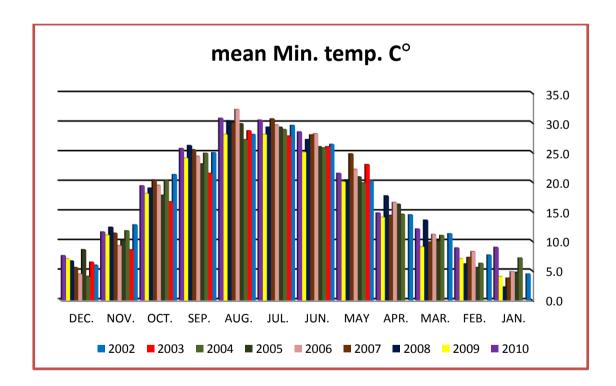


Fig. (2-3): The means annual of minimum temperature at Kirkuk for the periods from (2002-2010).

2.2 Rainfall

Rain works to purify the air of lots of solid and gaseous pollutants, as the rain has a significant impact on air pollutants during the dissolving of polluting gases of air (such as sulfur, nitrogen and carbon oxides) which is the most common gases in the atmosphere of the cities. Also, a large part of the suspended particles fall during the rain drops like dust particles, so it seems to clean the air through the fall rains. The rainfall in Iraq generally begins late in October, which is the first month of autumn and ends at the end of May which is the last month of spring where the rates are low in general (Hashim, 2009).

In the foothills and steppes south and southwest of the mountains suggest mean annual rainfall between 32 and 57 cm for that area. Rainfall in the mountains is more abundant and may reach 100 cm per year in some places (Iraqi Ministries of Environment and Water Resources, 2006). These annual rates of rainfall in the study area are diverse and tend to decrease, especially in recent years. This is what we notice in fig. (2-4), which shows the annual rates of rainfall in Kirkuk for the period (2002-2010), as it is obviously bimodal this distribution belongs to increasing in relative humidity and decreasing in temperature a companied with winter in Iraq.

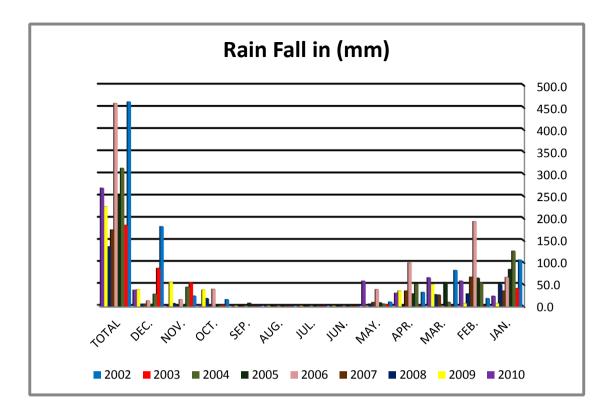


Fig. (2-4): The annual rates of rainfall at Kirkuk for the period from (2002-2010).

2.3 Relative Humidity

The relative humidity is the ratio between vapor pressure to the pressure of saturated steam at a certain temperature depending on temperature, the humidity decreases in summer due to high temperature and low rainfall, while the humidity increases 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 (Hashim, 2009).

The important effect of relative humidity is shown by reducing the concentration of pollutants in the air, as the water vapor works in the air to remove a large proportion of attached matter by various air pollutants. We note that decreasing rates of relative humidity in Kirkuk in recent years due to the high temperatures, as shown in the fig. (2-5), which

represents the annual rates of relative humidity in Kirkuk for the period (2002-2010).

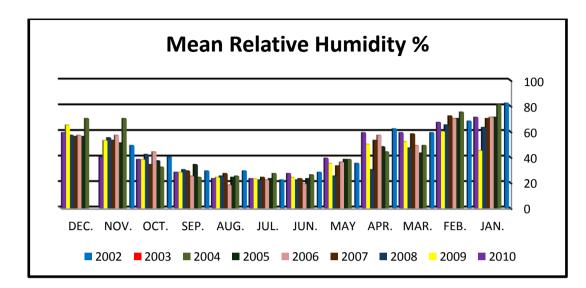


Fig.(2-5): The annual rates of relative humidity of Kirkuk for the periods from(2002-2010).

2.4 Wind Speed and Direction

The wind direction play an important role in the distribution of pollutants in air, moving pollutants released from various sources with the general direction of the winds prevailing, so the areas in the direction of the wind and carrying pollutants will bound to be more contaminated than the areas at opposite direction of the wind. When the wind speed increases the movement and spread of contaminants increase and therefore lack of concentration in the air.

The annual prevailing winds in the study area are mainly northwesterly and westerly winds (fig.2-7). They are blowing from the northwest towards the southeast, and are usually accompanied by dust storms and dust, especially in the summer. These winds can transmit pollutants from sources located in the north-west of the study area must therefore take into account wind direction at the sampling way. Figure (26) shows the annual rates of wind speed at Kirkuk for the period (2002-2010), fig. (2-7) shows the annual rates of wind direction using wind rose program.

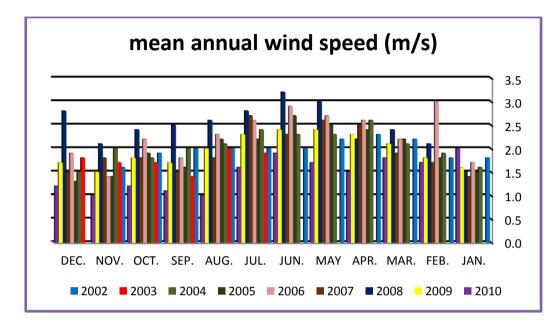


Fig. (2-6): The annual rates of wind speed at Kirkuk for the period from (2002-2010).

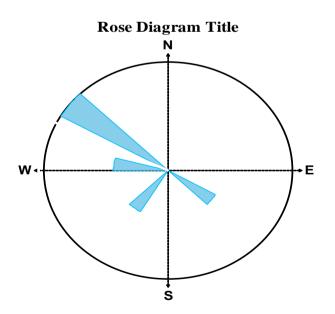


Fig. (2-7): The annual rates of wind directions at Kirkuk for the period from (2002-2010) using wind rose program.

Chapter Three

Methods and materials

3. Introduction

In this chapter the methods of operation and description for laboratory and field devices used in measurement and analysis are described and illustrated.

All the steps included in the processes and operations to measure the TSP and the gases concentrations (CO, $CO_2 NO_2$, SO_2) in the air as well as analyzing heavy metals (Pb, Cu, Ni, Cr, Cd), polycyclic aromatic hydrocarbons (the 16 US EPA priority) present in the environmental elements studied within the selected areas are described.

In order to assess the environmental pollution at Kirkuk oil refinery, and give an indication to the environmental impacts on the residential areas near and around it, 15 different sites inside and outside the refinery have been selected for ambient air and environmental sampling collection. Soil samples and plant samples of some perennial trees (Eucalyptus) growing in around these surroundings were collected for chemical analyses (heavy metals and polycyclic aromatic hydrocarbons). The Meteorological measurements of temperature, humidity, and wind speed at the sites of sampling were also measured.

Below is a description to the methodology and measurement steps and procedures that were followed in the field and laboratory tests in addition to a full description and illustration to the devises and tools that were used in those measurements.

3.1 Field works

The field works and activities included sampling of air, soil and plants, using portable field sampling and measuring equipments.

The most important part of any sampling process is the correct and accurate selection of site location to give the best results for environmental evaluation that can help in determining the impacts of the pollutants and their connection to their point of origin sources.

During the selection of the best sampling sites for air around Kirkuk oil refinery, the wind direction factor was taken into serious consideration as this factor has a remarkable effect on pollutants distribution. Site location was then selected in the different processing units inside the refinery and in areas near or around the refinery as well as in locations nearby residential sectors within Kirkuk city. The total numbers of sites selected are 15 sites in addition to another site outside Kirkuk city (Daquq Control) as a check and comparison site. Figure (3-1) spots the selected study locations on the regional map of the area.

In order to have the best descriptive effects of the effects of pollution on the environment caused by the pollutant sources (The Oil Refinery), samples of soil and plant were taken from the same sits that were tested for air pollution.

The testing sampling locations were selected at different distances around the refinery in different direction away from the refinery and that is to evaluate and to determine the most affected areas.

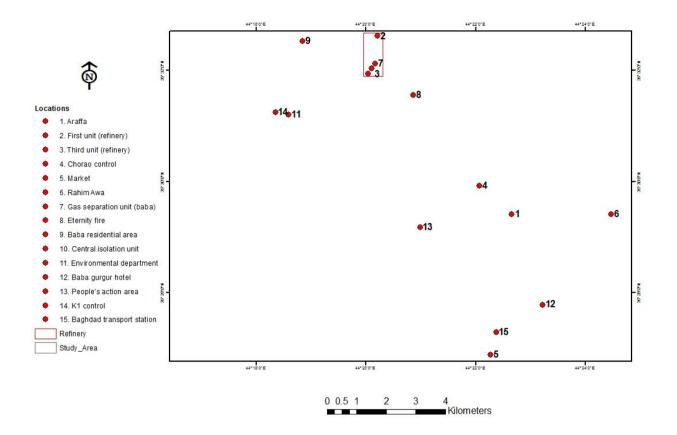


Fig. (3-1): GIS Map showing the selected locations of sampling sites at the study area.

Site no.	Name of the site	Latitude	Longitude
1.	Araffa	35° 28′ 84.6	044° 22′ 39.3 ⁻
2.	First Unit of Refinery	35° 31′ 97.3	044° 19′ 72.3
3.	Third Unit of Refinery	35° 32′ 01.8	044° 19′ 66.0
4.	Chorao Control	35° 29′ 55.5	044° 22′ 03.7 ⁻
5.	The Market	35° 26′ 53.1	044° 22′ 15.7
6.	Rahim Awa area	35° 29′ 24.7	044° 24′ 27.6
7.	Gas Separation Unit (Baba)	35° 32′ 06.9 [°]	044° 20′ 10.1 ⁻
8.	The Eternity Fire	35° 31′ 33.2 -	044° 20′ 51.3 ⁻
9.	Baba Residential Area	35° 32′ 31.6	044° 18′ 50.6
10.	Central Isolation Unit	35° 31′ 56.2	044° 18′ 50.6
11.	Environmental Department	35° 31′ 11.8	044° 18′ 35.3 ⁻
12.	Baba Gurgur Hotel	35° 27′ 47.2	044° 23′ 13.1
13.	Peoples Action Area	35° 29′ 10.7	044° 20′ 59.0 ⁻
14.	K1 Control	35° 31′ 14.4	044° 18′ 12.3 ⁻
15.	Baghdad Transport Station	35° 27′ 17.6	044° 22′ 22.3 ⁻
16.	Daquq Control (check point)	35° 07′ 03.5 ⁻	044° 27′ 06.3 ⁻

Table (3-1): Coordinates of the sampling sites by GPS.

3.1.1. Field Sampling Devices

1. CO, CO2 measuring device

To test the concentrations of CO and CO_2 a portable devise was used for testing, It is a field digital device produced by (TSI) company of an American origin holding the model number (IAQ-CALC 8762) which is designed to measure the concentration of carbon monoxide (CO) and dioxide (CO₂) concentrations in the air as per million unit (ppm). This devise has a sensor linked to it which enables the direct reading; the devise operates on batteries of (6 volt) voltage. Fig. (3-2) shows the image of this device.



Fig. (3-2): Mono and dioxide carbon (CO, CO₂) concentrations measuring devise

2. SO₂, NO₂ Measuring device

This devices produced by (Nova) company of Canadian as model (65690 RHTK) and model (613480 RHTK), were used to measure SO_2 and NO_2 concentrations in the air, this devise is a portable and it containing a sensor and a charger of (15 volt). The Device measures the concentrations of gases (H₂S, SO₂, and NO₂) in (ppm) unit. Figure (3-3) shows the device image.



Fig. (3-3): Image of device used in the measurement of (H₂S, SO₂, and NO₂) gases concentrations in the air.

3. Low Volume Sampler (Sniffer):

To examine samples for total suspended solids concentrations a low volume sniffer devise was used , the devise measures air samples taken from the sites at a rate of (liter /min) , this devise is equipped by (Rotheroe & Mitchll Ltd.) company of a (US origin). The type (L-30) of this devise consists of a filter holder circular form with a (6 cm) diameter it also includes a pump to pull and emptied air, measure the volume of air flow with a piece of transparent plastic installed in front of the device on the right side contains the small iron ball. The rate of air flow drawn that was used during testing varied from (40 - 70 liter/min). The type of filter used to hold the suspended solids in the air flow was a Whitman cellulose candidate of (6 cm) diameter. Fig. (3-4) shows the device features.



Fig. (3-4): Front and back view of Low Air Sampler (Sniffer) devise features.

4. An Anemometer

A digital an anemometer device was used in the field to measure the wind speed. This devises gives wind speed readings at a rate in (m /sec). It is of a Taiwanese origin, and a product of f (Lutron) company, model (Am-4221), and it runs with a battery of (6 volt). Fig. (3-5) shows this device.



Fig. (3-5): Anemometer devise used for measuring wind speed.

5. Air temperature and humidity measuring device

One of the main measurements that were taken during the study is air temperature and humidity; this was done using it a digital portable device. Temperature measurements in (C°) and relative humidity as a % were obtained from this devise which is of a Taiwan Origin, model (HT-3015HA) .The device has sensors linked to it and it has the capability to read directly, using a (9 Volt) battery . Fig. (3-6) shows the device, while the measurements of some climate elements are listed in tables (3-2, 3).



Fig. (3-6): the device that was used for the measurements of air temperature and humidity

Sample	Temperature	Humidity	Wind speed	Time of
no.	(C°)	%	(M/sec.)	sampling
1.	32.5	25	3	9.30 am
2.	35.1	13	8	1.10 pm
3.	37.6	12	6	2.15 pm
4.	32.5	27.1	3.1	9.30 am
5.	41.2	18.9	1.5	12.0 pm
6.	38	27.5	0.1	6.0 pm
7.	41.5	21.8	1.2	12.10 pm
8.	43	20.5	3.0	9.15 am
9.	42	26	2.0	10.45 am
10.	39.8	22.9	2.5	12.20 pm
11.	40.8	23.5	1.8	1.25 pm
12.	41	21.9	0.3	4.50 pm
13.	30	29.5	1.2	7.25 am
14.	31.5	33.5	0.4	8.35 am
15.	36.5	26	0.5	9.30 am
16.	40	22.3	2.8	11.0 am

Table (3-2): A list of the climate elements that were measurement atthe studied area in October 2010.

Table (3-3): A list of the climate elements that were measurement ofthe studied area during March 2011.

Sample	Temperature	Humidity	Wind speed	Time of
no.	(C ^o)	%	(M/sec.)	sampling
1.	27	12	1.5	2.10 pm
2.	21.4	17.8	5	9.30 am
3.	20.1	15.5	2.5	10.40 am
4.	22.7	11.2	3	1.20 pm
5.	22.8	11	2	2.30 pm
6.	24.5	13.4	0.7	9.05 am
7.	23.7	22.8	2.2	10.45 am
8.	19.5	28.5	3.5	9.35 am
9.	26.5	23.5	0.8	12.0 pm
10.	26.5	23.5	2.2	11.0 am
11.	24.5	29	1.2	1.15 pm
12.	11	29.9	2.0	7.20 am
13.	26.5	16	1.7	1.10 pm
14.	25,2	24	2.9	11.25 am
15.	23.9	20	1.5	9.50 am
16.	21.5	15	5	12.35 pm

After illustrating all the equipments and devises used for the measurement of different air pollutants, below is a description of the methodology and sampling procedures that was adopted to evaluate the pollutant concentrations.

3.1.2. Preparation of air samples:

Air samples were collected by Low Volume Air Sampler or what is mostly known as the (Sniffer) which collects the suspended particles in the air. Before the sampling collection process starts the Cellulose Filters is dried at a temperature of 80 c° in order to get rid of the moisture, and then weighed before being placed in the holder of the filters to get its inertial weight was (W_1) . This step is then followed by placing the Cellulose Filter in the device (in filter holder), and then calculating the size of the air flow once the startup and running of the devise. This latest value can be obtained by calculating the volume difference between the flow of air that iron ball read which is then represented as (V_1) , and the flow of air reading after the device runs for a period of one hour, which is represented by (V_2) . After that the Cellulose Filter will be taken and weighted again and the new weight is then represented as (W_2) . The concentrations of Suspended Particles then can be found by applying the below equation : .

(TSP)Concentrat ion =
$$\frac{(W_2 - W_1)}{V_T} \times 10^{-6} \dots \dots \dots (3-1)$$

Where:

TSP: concentration measured in unit microgram / m 3 (μ g/m3) W₂: weight of the filter after running the equipment (grams). W₁: weight of the filter before the running (grams) V_T: volume of air drawn with (m³)

 10^6 : Convert gram to a microgram .

The volume of air drawn V_T is calculated according to the equation:

$$V_T = \left(\frac{V_1 + V_2}{2}\right) \times \frac{t}{1000} \dots \dots (3-2)$$

where:

T: sampling time of total size per minute.

V₁: volume of air that iron ball recorded at the beginning of device playing.

V₂: volume of air that iron ball recorded at the end of device playing.

Fig (3-7) shows the process of air sampling at one of the studied



Fig. (3-7): Air sampling at one of the studied sites locations.

3.1.3. Preparation of soil and plant samples

The same pre chosen site location samples of soil specimens are collected, this sampling usually takes place at the same time when the air pollutants are measured. This is done by scraping the surface layer of the soil to depth less than 5 cm in thickness and for an area of approximately 1 meter square using a manual hand shovel, fig. (3-8) show this collection procedure.

Meanwhile plant samples (Eucalyptus tree leaves) will be collect from plants that grow and exist nearby the pre selected locations, figure (3-9) also shows the plant sampling method during this study.



Fig. (3-8): Soil sampling



Fig. (3-9): Plant sampling of eucalyptus tree

3.2. Laboratory works

After the collection of the samples from (air, soil and plant) they are taken to the laboratory for measuring the concentrations of different pollutants (heavy metals, poly aromatic hydrocarbons). This is usually done using the Atomic Absorption Spectrometry equipment which can determine the heavy metals concentrations, HPLC (High Performance Liquid Chromatography) and GC-MS (Gas Chromatography Mass) of the polycyclic aromatic hydrocarbon compounds.

Below is also an illustration and description of other laboratory devises and equipments that have been used for the evaluation of different pollutants concentrations.

3.2.1. Digestion method of air filters samples:

The method of digestion that was used during this study to the collected samples from the air is explained through the following points.

1- Cut the filter papers (air filter sample) into small pieces and placed in a Teflon beaker.

2 - Add an amount of 5 ml of nitric (HNO₃) acid to the shredded sample.

3 – Heat the sample using a heater till it approaches the solution of the drought.

4 – Remove the samples from the heater and leave it to cool.

5 - Add 3 ml of perchloric acid (HClO₄) to the cooled sample and re-heat it.

6 – Raise the sample before it dries and leave it to cool.

7 – Again add 2 ml of hydrofluoric acid (HF), and cover the sample and

leave it over night until the solution becomes clear.

8 – The sample is then filtered in a volumetric flask of 100 ml size.

9 - Complete the volume with deionized water to 100 ml and reserve the solutions in plastic containers until used.

While conducting those measurements a (Blank Solution) has to be prepared under the same conditions for the Treatment of samples and then this blank sample shall be subjected to the analysis process of the automation components. All the measurements then shall follow the formula below:

Metal Conc. $(\mu g/m^3) = C *Vi / V_T \dots Eq$ (3-3)

Where:

C: concentration of the element in the sample at (ppm) unit.

Vi: the size of the sample in ml unit.

VT: the total volume of air drawn size in cubic meters.

Similar to above digestion has to be made for samples taken from soil before testing with the atomic absorption, the digestive procedure of soil samples is illustrated in below.

3.2.2. Digestion method of soil samples:

The method of digestion of soil samples that has been widely used by other researchers (Page, 1982) was also applied in this study and this method can be obtained by the following steps:

1- Dry the soil samples from moisture and sieved using a 2 mm sieve size.

2 - Mix well and take a representative sample of the soil

3 – Weigh 1 g of the soil sample and place in a Teflon beaker.

4 - Add 5 ml of nitric (HNO₃) acid to the soil sample.

5 – Heat the sample using a heater till yellow fumes are formed and then it turns into white fumes.

4 – Raise the sample and leave it to cool.

5 - Add 3 ml of perchloric acid (HClO₄) and re-heat it till it turns out to yellow fumes.

6 – Cool the sample and then add 5 ml of hydrofluoric (HF) acid to it.

7 – Cover the sample and leave it over night until the solution becomes clear.

8 – The sample solution is then filtered in a volumetric of a 100 ml size.

9 - Complete the volume with deionized water and reserve the solutions in plastic containers ready for use.

3.2.3. Digestion method of plant samples:

In this study the following method of digestion was used.

1 - Dry the plant samples (leaves) at room temperature and then grind into a fine size.

2 – Weigh 1 g of the sample and placed it in a Teflon beaker.

3 - Add 5 ml of nitric acid (HNO_3) to the samples.

4 – Heat the samples using a heater until it escalate to yellow fumes and turn into white.

5 - Raise the sample and leave it to cool at room temperature.

6 - Add 3 ml of perchloric acid ($HClO_4$) to the sample and re-heat it.

7 - After the sample escalate to yellow fumes and turns into white raising sample leave it to cool.

8 – Filter the sample and complete the volume to 100 ml.

9- Reserve the obtained solutions in plastic container until used.

This method of digestion is mainly applied to the environmental research studies especially those done at the Environmental Research Center of the Ministry of Science and Technology.

3.2.4. Lab Devices

1. Atomic Absorption Spectrometer (AAS)

The device that was used to determine heavy metals concentration in solutions was of an American origin, it had a model number (AA-6200) and it was equipped for this purpose.

The device works on the appointment of the element concentration in the solution after it has been part of the evaporation of the solution through the heat of the flame gas acetylene up to more than (2000 C°). The Device is connected to a computer (Pentium 4) which allows the results to appear on the screen in digital or printed on thermal paper, fig. (3-10).



Fig. (3-10): Atomic Absorption Spectrometer (AAS) devise that was used during this study

To explain how to obtain concentration readings of pollutants from the collected samples using the atomic absorption spectrometer, it is important to illustrate the method of how digest and convert the samples so that they can be tested, this process is described below.

2- HPLC devise

The HPLC devise is used to measure the concentrations of PAHs concentrations which are extracted from the ecological samples (air. soil and plants), the model of the device that was used is (LC-2010A HT) of Shimadzu co, this is of a Japanese manufacture origin (fig. 3-11).

The main features and components of the HPLC system are listed in pullet points below:

1 - Solvent Reservoirs

This is a conical flasks (two numbers) with a capacity of one-liter of storage that is equivalent for the mobile phase related to pipes (PTFE), at the end of those pipes a porous filters diameter (0.2-0.5 μ m) is installed to prevent the passage of insoluble particles and impurities, pipes transferred the mobile phase to the pumping system.

- 2 Pumping System
- 3 Connecting Tubes
- 4 Sample Injection System:

In which standard solutions and samples are injected to the column using a syringe (injector) particular to HPLC.

5 – A Column:

A Column was used during this study to separate the poly aromatic hydrocarbon compounds of Phenomenex. This Colum is of an American company origin and is made out of stainless steel holding a dimension of (25 cm x 4.6 mm).

6 - Column Oven

7 - Detectors:

The detectors that used were very sensitive to low concentrations (parts per billion (ppb)), the UV detector and the wavelength of 254 nm was used in this study.

8 – A System Control Unit

A System control unit was used to control the conditions of the column temperature, wavelength and the rate of mobile phase speed.

9 – A computer.

It shows the chromatograms on the screen and the measurement of several factors on registration paper. Those output readings include retention time, area and height of beam readings and concentration which can both be illustrated at the same time also the computer can store this data on its hard or it can be taken using a flash memory at any time. (Fig. 3-11) shows the alignment and connections of these different devise elements.



Fig. (3-11): HPLC devise elements.

To compare concentration values obtained and to make sure that the results obtained are correct and with as little error as possible some of the samples were analyzed at the Appling Geosciences Institute laboratories – Technology University- Darmstadt/ Germany to determine PAHs concentration using the GC-MS device. (Fig. 3-12) shows the devise that was used in Germany.



Fig. (3-12): Image of the GC-MS devise at the Geosciences Institute laboratories – Technology University- Darmstadt/ Germany .

3.2.5. Chemicals used:

- To determine heavy metals the acids used were nitric acid (sigma Aldrich co.), perchloric acid (Thomas Baker) and hydrofluoric acid (Loba chemie) to digest the samples of air filters, soil and plant samples.
- 2- Polycyclic aromatic hydrocarbons used standard high purity of not less than 99.5% of the company (Sigma- Aldrich). A mixture of the 16 compound with a different concentration for each standard materials , (Naphthalene , Acenaphthene , Acenaphthylene , Fluorene , Phenanthrene , Fluoranthene, Chrysene, Anthracene , Benzo (a) anthracene, Benzo (k) fluoranthene, Benzo (b) Fluoranthene, Pyrene, Dibenzo (a, h) anthracene, Benzo (a) pyrene, Benzo (g, h, i) perylene , Indeno (1,2,3-cd) Pyrene,). The table (3-

4) showed the concentrations of these compounds with retention time of them.

- 3- Organic solvents used for extract poly aromatic hydrocarbons from environmental samples were dichloromethane (from Fluka chemika German), methanol (from Gainland Chemical Company GCC. UK)
- 4- Use deionized water throughout the experiments.

Use the moving phase (Acitonitryle - water), within the sequential recovery program (Gradient Elution) With rate flow of 0.5 ml/min at room temperature. as shown in table (3-4):

Table (3-4): the recovery program of moving phase (Acitonitryle - water) used to detect

CH ₃ CN %	Time (min.)
40	0
40	2
100	20
100	30
40	31
Stop	32

PAHs in this study.

3.2.6. Extraction method of PAH's from air filters:

Polycyclic aromatic hydrocarbons compounds extracted of air samples filters by a separating funnel where they placed with 20ml of a mixture of methanol and dichloromethane at a ratio of 1:1(Husain 2003). After that

separating funnel placed in the Shaker for a period of (12 hrs) to ensure that dissolve the polycyclic aromatic compounds in a mixture of solvents. After the extraction process end concentrated the samples in a rotary till drying and then add 1 ml of methanol to the samples and reserved in small containers till used.

3.2.7. Extraction methods of PAH's from soil and plant samples:

The extraction method used was applied by (Husain 2003) to extract PAHs from the environmental samples as follow: 1- grinding the samples to small size (100 μm).

2 - The samples placed in an oven at temperature (80-90°C) to get rid of moisture.

3-Wigh 15 gm. of the sample, put in a Cellulose Thumble and then in their place at Soxhlet Apparatus.

4- A mixture (180 ml) of methanol and dichloromethane as a 1:1 ratio, the extraction continuous to (20-24 hours) at the boiling point of the solvents.

5 - The sample has been conducted by a rotary evaporator to less than1ml was complete volume to 1 ml.

Table (3-5) represent the retention time and the concentrations of standards used in this study, fig. (3-13) represent the chromatogram of standards mixture for 16 EPAs priority PAHs by using HPLC device. While the table (3-6), fig. (3-14) represent the retention times, concentration of PAHs and chromatogram of the standards by using GC-MS device.

Table (3-5): Retention time and concentration of standards mixturefor the PAHs detected by HPLC.

No.	PAHs	Retention	Concentration
		time (min.)	(ppb)/3
1.	Naphthalene	2.852	500
2.	Acenaphthylene	11.329	500
3.	Acenaphthene	12.362	1000
4.	Fluorine	13.702	100
5.	Phenanthrene	14.144	40
6.	Anthracene	15.243	20
7.	Fluoranthene	16.410	50
8.	Pyrene	17.450	100
9.	Benzo(a)anthracene	18.350	50
10.	Chrycene	20.983	50
11.	Benzo(b)fluoranthene	21.796	20
12.	Benzo(k)fluoranthene	23.839	20
13.	Benzo(a)pyrene	25.318	50
14.	Dibenzo(ah)antracene	26.801	200
15.	Benzo(ghi)perylene	29.118	80
16.	Indino(1,2,3-cd)pyrene	31.243	50

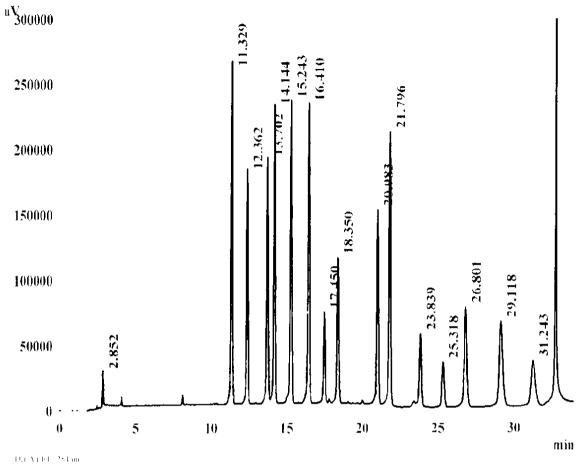


Fig. (3-13): HPLC Chromatogram of standard mixture for 16 EPA priorities PAHs.

No.	PAHs	Retentiont(min)	time	Concentration µg/L
1.	Naphthalene	8.385		40.915
2.	Acenaphthylene	10.421		40.915
3.	Acenaphthene	10.660		40.915
4.	Fluorine	11.301		40.915
5.	Phenanthrene	12.622		40.915
6.	Anthracene	12.706		40.915
7.	Fluoranthene	15.181		40.915
8.	Pyrene	15.900		40.915
9.	Benzo(a)anthracene	22.549		40.915
10.	Chrycene	22.793		40.915
11.	Benzo(b)fluoranthene	32.452		40.915
12.	Benzo(k)fluoranthene	32.587		40.915
13.	Benzo(a)pyrene	33.712		40.915
14.	Indino(1,2,3-cd)pyrene	37.933		40.915
15.	Dibenzo(ah)antracene	38.125		40.915
16.	Benzo(ghi)perylene	39.024		40.915

Table (3-6): Retention time and concentration of standards mixturefor the PAHs detected by GC-MS.

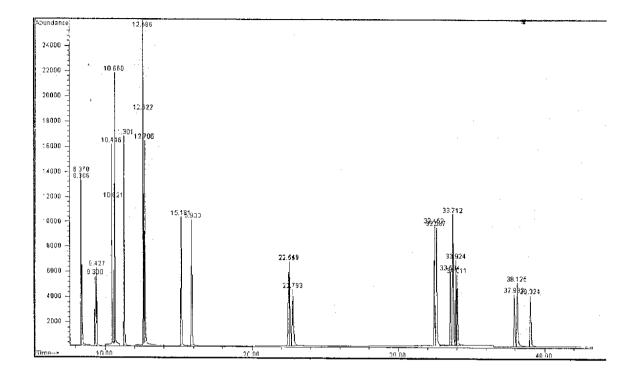


Fig. (3-14): GC-MS chromatogram of standards mixture of PAHs compounds.

3.3. Precision and Accuracy:

To ensure the accuracy and validity of analysis obtained, calculations of accuracy and precision are made. The inaccuracy may arise due to the devices and chemicals that were used in the measurements and sample preparations in addition to the methods of sampling and analysis, so there are no absolute precision measurements of any of the chemical analysis done.

Calculation of error reduction and prevention are illustrated below:

Accuracy:

Accuracy is known as the amount of compatibility between the value obtained from the analysis of the standard sample and the real values obtained (Maxwell, 1968). The resulting numerical difference of these two values can then represents the amount of error in the analysis. Equation (1) below explains how this value can be calculated using different available variables.

Accuracy= $\frac{2S}{X} \times 100$ Eq (1)

When the confidence level 95%

$$\mathsf{S}=\sqrt{\frac{\sum (Xn - \overline{X})^2}{N}}$$

Where:

N = number of analysis times = 3

 $\mathbf{S} =$ standard deviation

X1, X2, X3 = (Xn) = results of chemical analysis

Pb Accuracy = $\pm 11.39\%$ (when the confidence level 95%)

Cu Accuracy = \pm 9.22% (when the confidence level 95%)

Ni Accuracy = \pm 5.97% (when the confidence level 95%)

Cr Accuracy = $\pm 10.5\%$ (when the confidence level 95%)

Cd Accuracy = \pm 9.0% (when the confidence level 95%)

Precision:

Precision can be defined as the compatibility between different readings resulting from the appointment of the content of a particular part in what form (Maxwell, 1968).this important numerical value can be obtained from eq (2) in below. **Precision=** $\frac{2S}{X} \times 100$ Eq (2)

$$\mathsf{S}=\sqrt{\frac{\sum (Xn-\overline{X})^2}{N}}$$

 \mathbf{N} = number of analysis times

X= analysis Rate

 $\mathbf{Xn} =$ result of chemical analysis

 $\mathbf{S} =$ standard deviation

from above Precision value for different elements can be then evaluated as follows.

Pb Precision = \pm 8.59% (% 95 when the confidence level)

Cu	Precision	=	\pm	12.8%	when	the	confidence	level	95%)
Ni	Precision	=	±	8%	(when	the	confidence	level	95%)
Cr	Precision	=	±	9.2%	(when	the	confidence	level	95%)
Cd	Precision	=	\pm	7.56%	(when	the	confidence	level	95%)

3.4. Data Analysis and Fitting Model

In this part of the research: assessing, examining, and analyzing the produced data from the chemical analyses are made using software programs such as Arc GIS for modeling the distribution of pollutants in air, soil and plants.

Drawing maps of air, soil and plant pollution for the studied area will be accomplish indicating maximum and minimum and average of each analyzed variable to determine the most affected area by the refinery pollutants emitted. Least significant difference (LSD) test was used to compare the significant difference between means of heavy metals. Data were analyzed using statistical analysis system – (SAS 9.2).

Chapter Four

Results and Discussion

4. Introduction

This chapter illustrates the results obtained for pollution measurements of (TSP, Gasses, heavy metals and polycyclic aromatic hydrocarbons) in air, soil and plant of the studied area in Kirkuk Oil Refinery and surrounding areas using the Arc GIS 10 program. Also the chapter discusses those results and compares the findings with allowable slandered international limits and evaluates the pollution levels recorded.

The use of the Arc GIS 10 program allowed plotting the recorded data in maps and representing those pollutants all over the measured site areas.

In this chapter pollutants have been measured in air, soil and in plants were at each of the above environmental elements certain types of pollutants have been measured and studied. Below is the representation of those findings.

4.1 Air pollution

Urban air pollution is an environmental problem in many countries. The sources of urban air pollution emanate mostly from combustion activities originating mainly from automobiles and industrial activities. . These combustion activities release numerous air pollutants that are toxic to both the environment and to humans. Among of those many air pollutants released are, polycyclic aromatic hydrocarbons (PAHs), suspended particulate matter (SPM) and carbon monoxide (CO) (Taylor & Nakai 2012).

Air pollution is considered as one of the severe problems the worlds facing today. It deteriorates ecological condition and can be defined as the fluctuation in any atmospheric constituent from the value that would have existed without human activity. Over the years there has been a continuous increase in human population, road transportation, vehicular traffic and industries which has resulted in further increase in the concentration of gaseous and particulate pollutants released to the environment (Seyyednejad, 2011).

The air we breath 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 (Masitah et al, 2007).

4.1.1 Total Suspended Particles:

Suspended particle solids, which are air pollutants stuck in the air with a small volume ranges between (0.01-200) Microns (WHO, 1996). TSP was the first indicator used to represent suspended particles in the ambient air (Masitah et al, 2007). 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 (Harrison, 1992; in alsaadi 2012). 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. (Al-Saadi 2012; Hashim 2009).

The particles, with a diameter bounded by the range of $(1-10 \ \mu m)$, 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 (Ahrens, 2005). 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 (Al- Maliky 2006).

Table (4-1): Local and global standard of some air pollutants(Ministry of Environment - Air Pollution Department for the year
2008.

No.	Air Pollutants	World Limits WHO	National Limits
1	Carbon monoxide	8 hour / 10 mg/m ³	/hour 35 ppm
	CO ppm	hour / 9 ppm	8 hour / 9 ppm
		year/100 mg/m ³	
2	Nitrogen Dioxide	hour /0.11 ppm	hour 0.25 ppm/
	NO ₂ ppm	24hour / 150 μg/m ³	year/ 0.05 ppm
		year/ 40 µg/m ³	
3	Sulfur Dioxide	hour/ 0.01 ppm	hour / 0.14 ppm
	SO ₂ ppm	year/ 0.03 ppm	year / 0.002 ppm
4	Total Suspended particle	hour/ 150 μg/m ³	hour 24 / 350 μg/m ³
	TSP μg/m ³	year / 60 -90 µg/m ³	year / 150 µg/m ³
5	Lead	year / 0.5-1 µg/m ³	hour 24 /2 μg/m ³
	Pb μg/m ³		year/ 1.5 µg/m ³
8	Carbon dioxide	250 ppm /hour	
	C O ₂ ppm		

The concentration averages of suspended particles (TSP) recorded in this study were significantly higher than the permissible allowable limits of the determinants of the Iraqi National standards (350) μ g/m³ and from the worlds international allowable limits (60-90) μ g/m³ (Table 4-1) for both of the periods of this study : October 2010 and March 2011. Where the averages were (818.94 μ g/m³ and 829.89 μ g/m³) respectively. It was also observed that the TSP concentrations increased at the direction away from the refinery (fig.4-1) mostly at the south east direction that coincides with the prevailed wind direction at the studied area as it was referred to in chapter two.

The maximum value recorded for TSP during October was at the Eternity fire $(2371.8\mu g/m^3)$ which is due to the presence of the gas flares of the refinery nearby in addition to the Eternity Fire itself. On the other hand the minimum value was at the Chorao Control site $(192.3\mu g/m^3)$ as shown in table (4-2) and figure (4-1). In March period the maximum recorded value was at Baghdad transport station (3555.6 $\mu g/m^3$) due to traffic intensity at this site, while the minimum value was at the Central Isolation Unit at the refinery and the Environmental Department of the Northern Oil Company (229.9 $\mu g/m^3$) as it is shown in table (4-2) and figure (4-1). The little difference between the two periods reflects the little effect of the seasonal changes.

Sa. No.	TSP. in October	TSP. in March	The site name
	(µg/m ³)	(μg/m ³)	
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.	1635.22	2068,9	RahimAwa
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.	1234.57	3555.6	Baghdad transport station
16.	254	526.3	Daquq control
Mean	818.94	829.89	
Iraqi National	350 μg/m ³	350 μg/m ³	
standards			
World	60-90 μg/ m ³	60-90 μg/ m ³	
international			
allowable			
limits			

Table (4-2) TSP concentrations in the studied area and comparisonwith values of national and world limits.

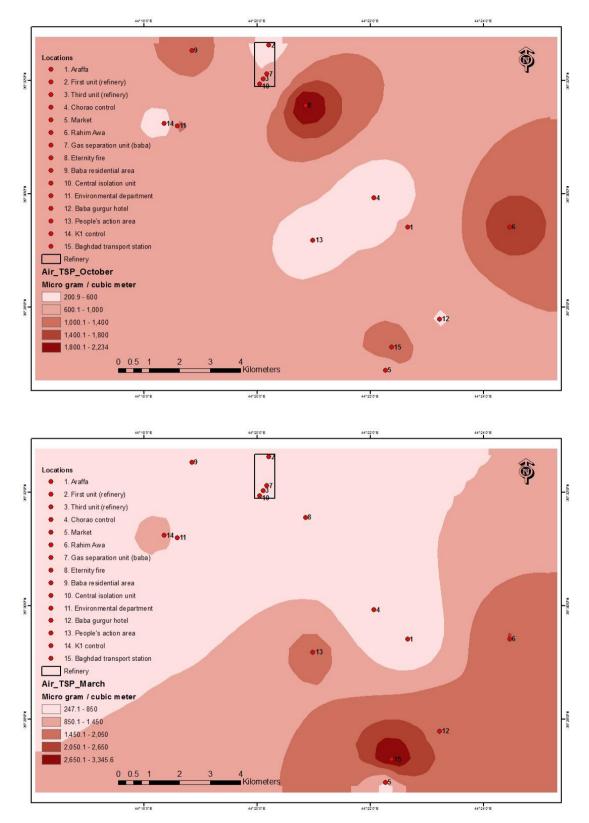


Fig. (4-1): Total suspended particles distribution in air of the studied area in October 2010 and March 2011.

4.1.2 Gasses

Air pollution concentrations in urban areas vary in both time and space. Time variations are strongly influenced by changes in human activities. Several activities occur repeatedly at regular intervals thus producing cycles in air pollution changes, like daily variations in CO concentration due to the change in traffic density or seasonal variations in air pollution (Fugas 1991).

The most diffused and harmful pollutants in industrial area are Sulfur Dioxide (SO₂), Nitrogen Oxides (NO_x), Carbon Monoxide (CO), troposphere ozone (O₃) and heavy metals, as well as suspended particulate matter (Assadi et al 2011).

Some of those harmful gases are measured and studied in this research, below the findings as to their concentrations.

4.1.2.1 Carbon Monoxide (CO)

The mean values of concentrations of CO recorded in the studied areas in October was 2.694ppm with a maximum value of 14.1ppm at site no. 5 (the market) and the minimum value was 0.0 at some other sites as shown in table (4-3).

All the maximum values were recorded at locations far from the refinery (fig. 4-3). This reflects that the refinery emission of CO is lower than the other factors such as vehicles and power plants.

The mean concentrations of CO in March were 1.956ppm with a maximum value of 7.5ppm at site no.15 (Baghdad transport station) and a minimum value of 0.0 at some other sites as shown in table (4-4), the high values reflects the effect of vehicle exhausts and their emissions in the air.

Comparing the above results it is found that the averages of CO obtained are lower than what is allowed in the national and international

worldwide limits and for both of the study periods October 2010 and March 2011 tables (4-3, 4).

4.1.2.2 Carbon Dioxide (CO₂)

Carbon dioxide concentrations are found to be higher than of those allowed in the national and international world limits (250ppm) and for all of the periods and at all sites of the studied area.

The highest concentration was in October (495ppm) at site no.5 (market site) and the lowest concentration was (297ppm) with an average of (375.25ppm) (table 4-3). Furthermore the highest concentration of CO_2 was in March (341ppm) at the site no. 8 (The Eternity Fire) near the gas flares and the lowest concentration was (251ppm) with an average of (303.19ppm) (table 4-4).

The difference between the two periods reflects the effect of meteorological conditions especially the effect of rainfall. The increasing CO_2 concentration at the studied area is due to the fuel combustion operation of gas flares at the refinery and vehicles and power plants, then inturn lead to increase in air temperature. This finding agrees with Hashim (2009).

4.1.2.3 Nitrogen Dioxide (NO₂)

The results of NO₂ at the studied area (tables 4-3, 4) show that the average values are slightly higher than the allowable national and international limits (0.25 and 0.11ppm) respectively and for both of the periods, where the average of NO₂ during October 2010 was (0.75ppm) with a maximum value of (1.4ppm) at site no.15 (Baghdad transport station) and the lowest value was (0.0ppm) at some other sites.

This increase in concentration is due to fuel combustion operation of vehicles.

On March 2011 the average value recorded was (1.159ppm) with a high value of (1.4ppm) at two different sites (site no.2&10 which represent the refinery sits) and the lowest value was (0.7ppm). The increase in concentration at the refinery sites was a result of the increase in production operations during those periods which had led to an increase in the combustion.

4.1.2.4. Sulfur Dioxide (SO₂)

SO₂ measurements were taken at some of the selected site locations. This was done using portable devises the results of those tests showed that the concentration of SO_2 in the air in October 2010 is slightly higher than what is permitted and allowed in the worlds standard limitations which should not exceed the level of (0.01ppm for exposure of one hour) for SO_2 concentrations, yet they are lower than the national limitation (0.14ppm for exposure of one hour). The average of SO_2 is (0.075ppm) with a maximum value of (0.4ppm) at site no.4(Chorao Control) and a minimum value of (0.0ppm) at various other sites of the studied area these results are illustrated in (table 4-3). During March 2011 no record of any concentration of SO₂ was made except of one site (0.1ppm) at site no.8 (The Eternity Fire site) which locates near the gas flares and this can be considered normal as the site is very close to the flares.

The decreasing of SO_2 concentration at this period reflects the effect of meteorological conditions especially during rain fall.

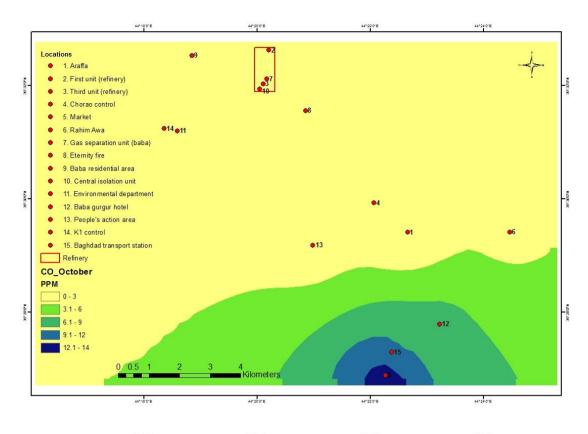
Table (4-3): Gasses concentrations measurements in the sites of

studied area (ppm) in October period 2010.

Sa. No.	CO (ppm)	CO ₂ (ppm)	NO ₂ (ppm)	SO ₂ (ppm)
1.	n.d.	304	n.d.	n.d.
2.	n.d.	304	n.d.	n.d.
3.	n.d.	295	n.d.	0.3
4.	1.7	297	n.d.	0.4
5.	14.1	495	n.d.	0.2
6.	2.4	478	0.8	n.d.
7.	1.5	385	n.d.	0.3
8.	n.d.	480	1.0	n.d.
9.	n.d.	450	1.2	n.d.
10.	n.d.	430	1.3	n.d.
11.	n.d.	335	1.2	n.d.
12.	6.5	390	1.2	n.d.
13.	1.7	308	1.0	n.d.
14.	1.2	305	1.3	n.d.
15.	9.0	354	1.4	n.d.
16.	5.0	394	1.6	n.d.
Mean	2.694	375.25	0.75	0.075
National standards	35 ppm	250 ppm	0.25 ppm	0.14 ppm
World standards	9 ppm	250 ppm	0.11 ppm	0.01 ppm

Sa.no.	CO (ppm)	CO ₂ (ppm)	NO2 (ppm)	SO2 (ppm)
1.	1.5	313	1.2	n.d.
2.	n.d.	275	1.4	n.d.
3.	4.5	297	1.2	n.d.
4.	1.7	323	1.2	n.d.
5.	1.5	313	1.2	n.d.
6.	0.7	251	1.2	n.d.
7.	1.0	291	1.3	n.d.
8.	1.5	341	0.7	0.1
9.	2.5	340	1.2	n.d.
10.	3.1	317	1.4	n.d.
11.	1.7	288	1.3	n.d.
12.	2.7	258	0.95	n.d.
13.	n.d.	312	1.3	n.d.
14.	n.d.	310	1.2	n.d.
15.	7.5	320	0.8	n.d.
16.	1.4	302	1.0	n.d.
Mean	1.956	303.19	1.159	0.006
National standards	35 ppm	250 ppm	0.25 ppm	0.14 ppm
World standards	9 ppm	250 ppm	0.11 ppm	0.01 ppm

Table (4-4): Gasses concentrations measurements in the sites ofstudied area (ppm) in March period 2011.



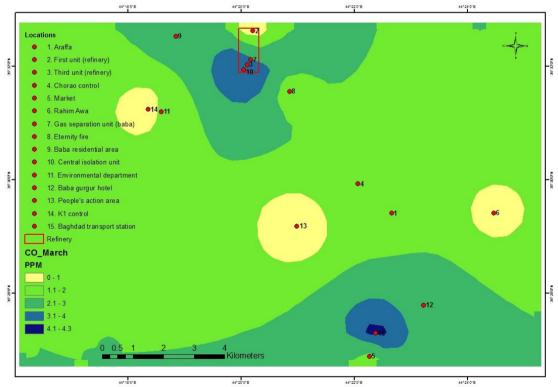


Fig.(4-2): GIS map showing CO distribution in air for the studied area for the period of October 2010 and March 2011.

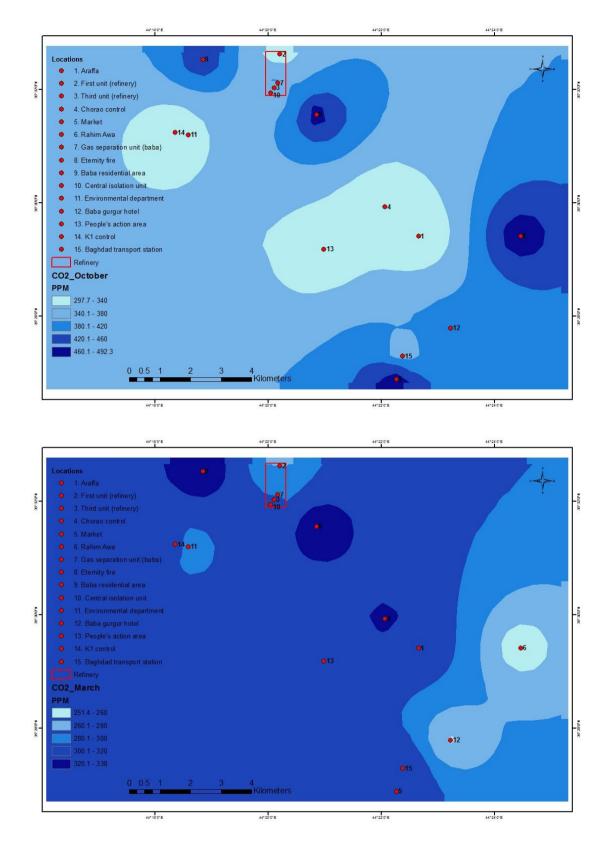


Fig. (4-3): GIS Map showing the CO₂ distribution in air at the studied area in October 2010 and March 2011.

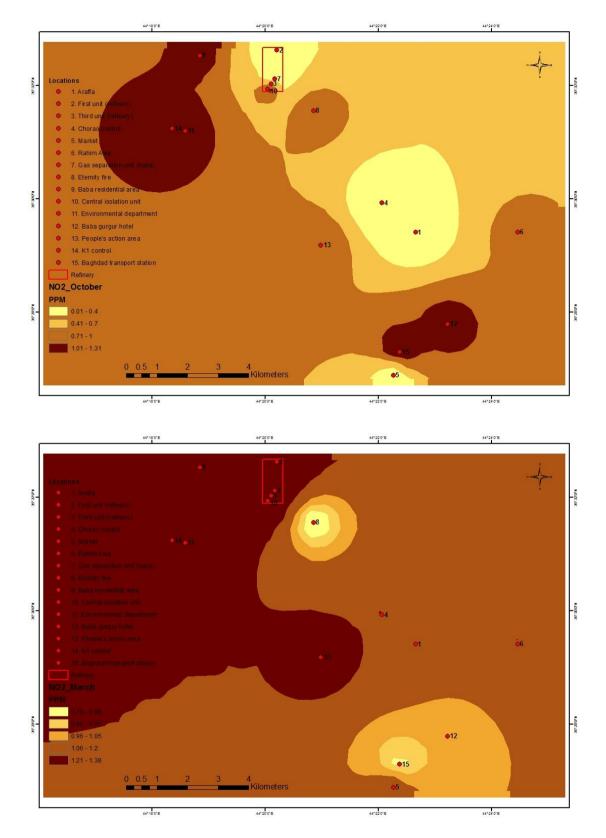


Fig. (4-4): GIS Map showing NO₂ distribution in the air of the studied area in October 2010 and March 2011.

4.1.3. Heavy metals

Heavy metal is types of pollutants that have a great potential harm to ecological environment. They usually cannot be biodegraded when released into the environment (Li et al 2010). 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); moreover chromium (VI) compounds can cause chrome ulcers, corrosive reactions on the nasal septum, acute irritative dermatitis, and allergic eczematous dermatitis among subjects who have been exposed to such pollutants . The toxicity of lead can also be largely explained by its interference with different enzyme systems; were results showed that lead inactivates these enzymes by binding to SH-groups of its proteins or by displacing other essential metal ions. (Leili, et al 2008).

During this study many samples from different sites were examined for different heavy metals concentrations and the results of those experiments and test are illustrated below.

Table (4-5): Global standard of the total suspended particles (TSP)

Air pollutants	Guideline	Average Time	Source
TSP	150µg/m ³	24 h	USA 1998
	60-75 μg/m ³	1 year	USA 2005
	60-90 μg/m ³	1 year	WHO 1996
	350 μg/m ³	24 h	Iraq 1992
Lead	0.5 μg/m ³	Annual	WHO 1996
	1.5 μg/m ³	3Months	USA 2005
	3.0 μg/m ³	24 h	Iraq
Chromium(Cr	4*10 ⁻²	Lifetime	WHO 1996
VI)	$(\mu g/m^3)^{-1}$		
Nickel	0.2 μg/m ³	Lifetime	WHO 1996
	3.8 *10 ⁻⁴		
	$(\mu g/m^3)^{-4}$		
Cadmium	0.05 μg/m ³	Annual	WHO 1996
Cadmium	5 μg/m ³		
(deposition)			
Copper	0.257	-	WHO 1995

and trace elements (Al-Saadi 2012)

4.1.3.1. Lead (Pb)

The concentration of lead in the air of the studied area in October gave mean values of $4.56 \ \mu g/m^3$ and records as high as $8.56 \ \mu g/m^3$ were recorded at sites such as site no.15 (Baghdad transport station) and as low as $0.86 \ \mu g/m^3$ at site no.5 (the market site) (table 4-6) show those findings . Comparison between those values and the national and world standard limits lead to the conclusion that what was recorded that most of the heavy metals are higher than those limits especially in those sites that had a high traffic density and fuel combustion operation.

Whereas the concentration of lead in March recorded lower values than the national and world limits($3\mu g/m^3$, $0.5\mu g/m^3$)

respectively, were the average was 0.045 μ g/m³ and the maximum value is 0.104 μ g/m³ at site no.14 (k1 control) and the minimum value is as small as 0.01 μ g/m³ at some other sites, this decreasing in lead concentration reflects the effects of meteorological conditions during this period.

4.1.3.2 Copper (Cu)

The concentration of Copper in air on October was $0.031\mu g/m^3$ in average with a maximum value of $0.072 \ \mu g/m^3$ and a minimum value of $0.002 \ \mu g/m^3$ and those readings are much lower than the world limits as observed in (table 4-5). Meanwhile copper concentration on march recoded an average value of $(0.115) \ \mu g/m^3$ and the maximum and minimum values of $(0.177 \ \mu g/m^3)$, $0.04 \ \mu g/m^3$) were spotted at site no.1 (Araffa site) and on sit no.5(the market site) respectively. Generally The concentration of copper during the two periods were lower than what the worlds standard allow.

4.1.3.3 Nickel (Ni)

It was found that Nickel concentrations were higher that the worlds allowable standard limitaions . The averages of Nickle during the two periods can be seen in (tables 4-5, 6) . From the table it can be seen that the verage concentarion during October was 0.627 μ g/m³ with a maximum value of 0.86 μ g/m³ at site no.4(Chaorao control).and was of an average of 0.474 μ g/m³ in March with a maximum and minimum values of 0.61 μ g/m³ and 0.27 μ g/m³ at site no.6(Rahim Awa) respectively. This decrease of concentration in March may be related to the meteorological conditions as well as the other factors.

4.1.3.4 Chromium (Cr)

Chromium concentrations were also investigated at this study and it was found that the average of Chromium in the air of the studied area in October was 0.233 μ g/m³ with a maximum value of 0.36 μ g/m³ in both sites no.4,15 and the minimum value 0.01 μ g/m³ was found to be in site no.12 (Baba Gurgur hotel).

Samewise the average values of Chromium concentrations in March were 0.745 μ g/m³ with a maximum value of 2.13 μ g/m³ at site no.14(K1 control) and a minimum value of 0.01 μ g/m³ in other sites. Table (4-6) and fig.(4-8) show the Chromuim investigation made in this study .

We can relate the increase of Chromium concentration in the air is due to the increment of the combustion fuel and expanded operations of the refinary during this period in addition to other related factors such as the exsistince of the private power generators that are active during this season due to the lack of national electricty.

4.1.3.5 Cademium (Cd)

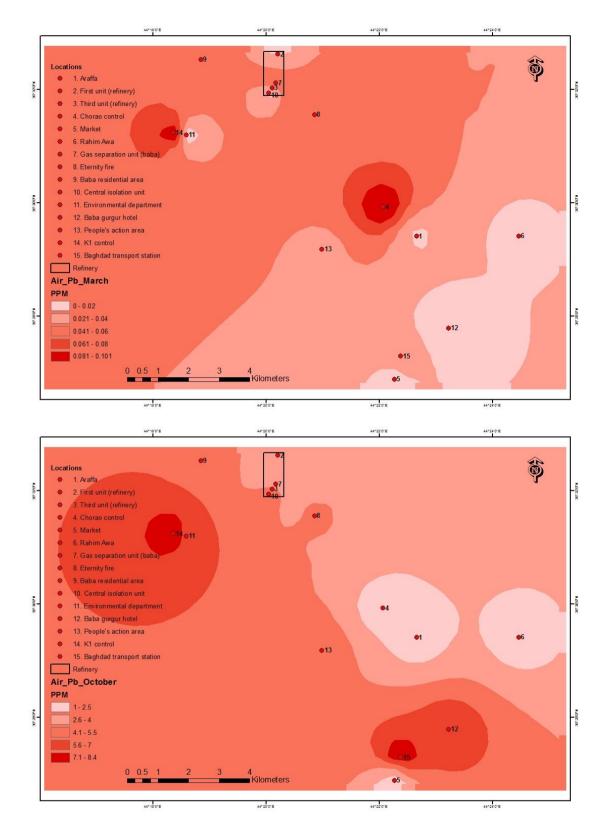
The other heavy meatal element that was studied was Cademium . From (tables 4-5 and 4-6) values as high as 0.18 μ g/m³ at site no.10 and as low as 0.031 μ g/m³ at site no.1 can be seen during October and values as high as 0.12 μ g/m³ at site no.14 and as low as 0.072 μ g/m³ at site no.9 during March . Meaning that the average values were 0.095 μ g/m³ and 0.096 μ g/m³ for October 2010 and March 2011 respectively. This slight difference between the two averages proves that there is no effect of season changes on the concentration of this element .

Pb Cu Ni Cr Cd Sample No. $\mu g/m^3$ $\mu g/m^3$ $\mu g/m^3$ $\mu g/m^3$ $\mu g/m^3$ 1 1.45 0.006 0.82 0.25 0.031 2 3.530 0.051 0.53 0.14 0.08 3 0.94 0.033 0.67 0.15 0.06 4 1.60 0.039 0.86 0.36 0.074 5 0.86 0.02 0.69 0.37 0.097 6 1.73 0.043 0.604 0.280 0.06 7 0.012 0.282 3.08 0.65 0.108 8 4.17 0.003 0.46 0.31 0.132 9 5.03 0.002 0.63 0.23 0.16 10 6.43 0.005 0.46 0.08 0.18 11 5.64 0.046 0.65 0.330 0.04 12 6.99 0.025 0.67 0.01 0.06 13 5.24 0.049 0.56 0.126 0.09 14 8.61 0.021 0.56 0.23 0.09 15 8.65 0.072 0.606 0.36 0.104 16 9.08 0.069 0.61 0.03 0.023 4.56 0.031 0.627 0.233 0.095 mean national $3\mu g/m^3$ 0.25 µg/m³ $0.2 \,\mu g/m^3$ world $0.5\mu g/m^3$ LSD (p<0.05) 0.3705 0.0156 0.0648 0.047 0.0204

Table (4-6): Heavy metals concentrations in the air of the studied area inOctober 2010.

Pb Ni Cr Cd Sample Cu µg/m³ $\mu g/m^3$ µg/m³ μg/m³ No. µg/m³ 1 0.015 0.01 0.177 0.61 0.108 2 0.013 0.119 0.49 0.01 0.077 3 0.086 0.143 0.58 0.102 0.02 4 0.102 0.144 0.57 0.01 0.108 5 0.011 0.04 0.48 0.082 0.01 6 0.013 0.087 0.27 0.03 0.079 7 0.057 0.078 0.38 1.44 0.106 0.051 0.102 0.393 8 1.06 0.08 9 0.055 0.101 0.51 0.01 0.072 10 0.01 0.05 0.39 0.01 0.108 11 0.01 0.11 0.60 1.57 0.085 12 0.01 0.161 0.49 0.41 0.074 0.034 0.141 0.074 13 0.48 2.11 14 0.104 0.075 0.48 2.13 0.12 15 0.037 0.095 0.35 0.60 0.10 16 0.109 0.217 0.520 2.49 0.16 mean 0.045 0.115 0.474 0.745 0.096 national ۳µg/m³ $0.5\mu g/m^3$ 0.25 μg/m³ $0.2 \,\mu g/m^3$ world LSD (p<0.05) 0.1309 0.0207 0.0229 0.0625 0.0271

Table (4-7): Heavy metals concentrations in the air of studied area inMarch 2011.



Fig(4-5): GIS map showing Lead (Pb) distribution in air of the studied area in October 2010 and March 2011.

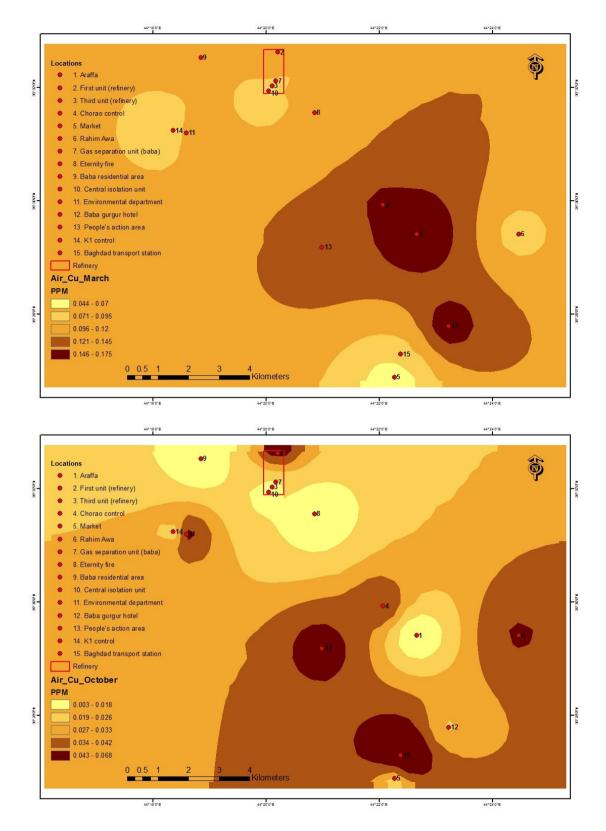
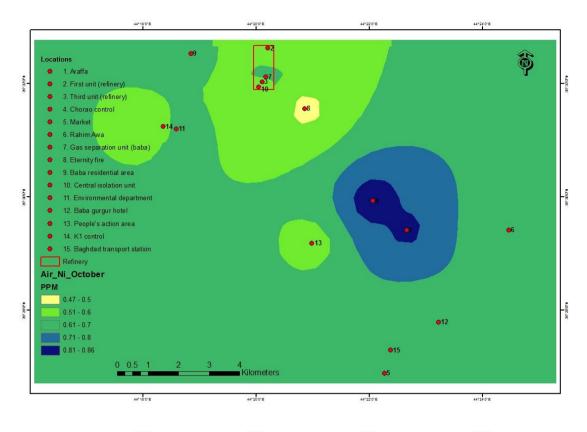


Fig.(4-6): GIS map showing Copper (Cu) distribution in air of the studied area in October2010 and March2011.



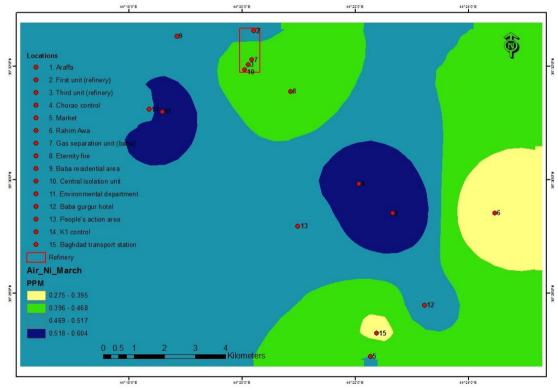


Fig.(4-7): GIS Map of Nickel distribution in air of the studied area for the two periods of the study .

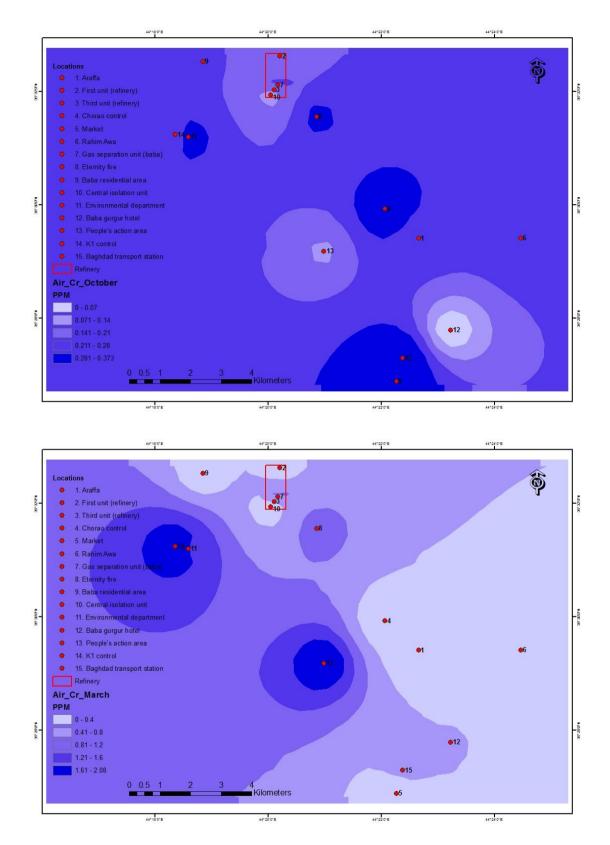


Fig.(4-8): GIS map showing Chromium distribution in air of the studied area in october 2010 and march 2011.

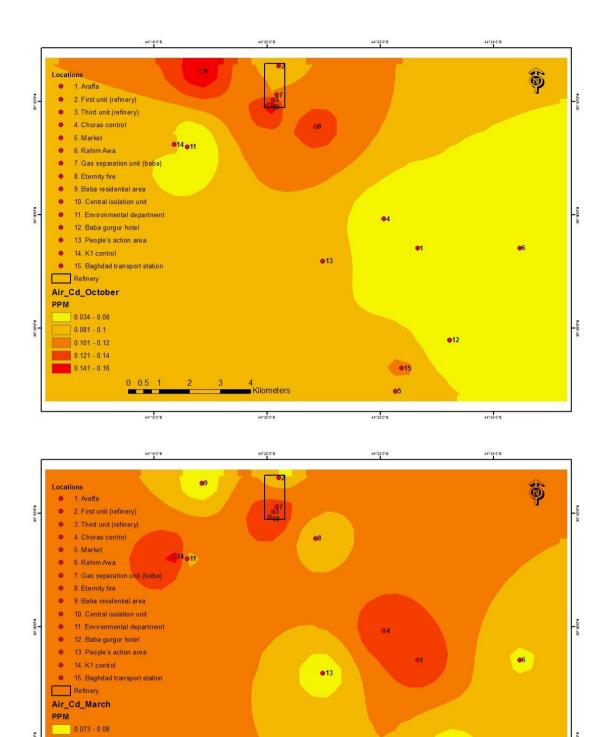


Fig. (4-9): GIS map for Cadmium distribution in air of the studied area in October 2010 and Marc 2011.

Kilometers

44-20/0'E

@12

44°24'0'E

015

44-220 E

N DEC SE

0.081 - 0.09

0.091 - 0.1 0.101 - 0.11 0.111 - 0.114

0 0.5 1

44° 15'0'E

4.1.5. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a family of 660 chemical compounds with a molecular structure consisting of at least two fused aromatic (benzene) rings. They are predominantly formed as a result of the incomplete combustion of organic fuels such as the burning of coal, petroleum, oil and wood (Jan et al, 2000; Bari et al 2011; Halek et al, 2006). Those combustion sources include emissions from automobiles, industrial processes (Petrochemical industry and manufacturing of paints) and lacquers (Zitka et al 2012; Ding et al 2007) . Other sources also include domestic heating system, waste incineration facilities, tobacco smoke, and several natural sources including forest fires and volcanic activity as part of combustion sources.

Human exposure to polycyclic aromatic hydrocarbons may occur through food, water, air and through direct contact with materials containing PAHs. The United States environmental protection agency (US EPA) has identified 16 different PAHs being as "priority pollutants" because they have stronger toxicity than others. (Shihua et al 2001). PAHs are distributed in air, soils, waters, and even in river and ocean sediments and sludge all over the world (Zitka et al 2012). Many Studies have been made to Polycyclic Aromatic Hydrocarbons (PAH), associated with combustion and ambient aerosols, because of their carcinogenicity and mutagenecity in animal and bacterial assay tests (Venkataraman et al.2002; Xie et al 2003).

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds. They have a relatively low solubility in water, but are highly lipophilic. Most of the PAHs with low vapor pressure in the air are adsorbed on particles.

When dissolved in water or adsorbed on particulate matter, PAHs can undergo photo decomposition when exposed to ultraviolet light from

solar radiation. In the atmosphere, PAHs can react with pollutants such as ozone, nitrogen oxides and sulfur dioxide, yielding diones, nitro- and dinitro-PAHs, and sulfonic acids, respectively. PAHs may also be degraded by some microorganisms in the soil (WHO 2000). Occupational Safety and Health Assembly (OSHA) set limits of allowable PAHs in the atmospheric air to (0.2 mg/m³) (Hussain, 2003).

Depending on their molecular weight (which is inversely related to their vapor pressure), PAHs in ambient air can be found in the gas-phase (e.g., 2-ring naphthalene), particulate phase (e.g., 5-ring benzo[a]pyrene), or will partition between gas- and particle- phases (e.g., 3-ring phenanthrene and 4-ring pyrene) (Dzepina et al, 2007), fig. (4-10) shows the molecular structure of these compounds.

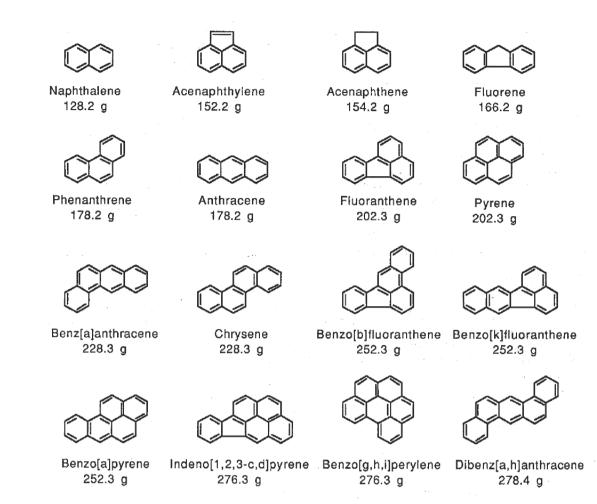


Fig. (4-10): Molecular structure of the 16 polycyclic aromatic hydrocarbons (PAHs) selected as priority pollutants by the American Environmental Protection Agency (EPA). (Henner et al 1997).

Atmospheric PAH are partitioned between the gaseous and the particulate phases, but the carcinogenic 5- and 6-ring constituents are chiefly linked to particles (Alves et al 2009; Tang et al 2006)

The maximum concentration of PAHs in air of the studied area in October as a total was $67.685\mu g/m^3$ in site no.2 (The First Unit of Refinery) meanwhile the minimum concentration was $0.028\mu g/m^3$ in site no.5 (The Market). As shown in (table 4-7) the 16 EPAs priority PAHs detected in the studied area were not all found at all sites of measurements due to their physicochemical properties of these compounds.

As a result naphthalene was detected in refinery and the sites nearby due to the low molecular weight found in gas phase compared with the compounds of high molecular weight found in particulate phase detected in the far away sites from the refinery such as benzo(b) flouranthen, benzo(k) flouranthen, benzo(a)pyrene, etc..

The concentration of PAHs in air of the studied area in March was rather high (7924.27 μ g/m³) in site no.6 (Rahim Awa), while the lowest concentration was detected to be (0.155 μ g/m³) at site no.12 (Baba Gurgur Hotel). This increment in PAHs concentrations at this period can be referred to the increase of fuel combustion operations as a result of increasing production operations of the refinery and the other factors such as the power plant. Appendix (1) represent HPLC & GC-MS Chromatograms of PAHs in the Air of the Studied Area at the Two Periods.

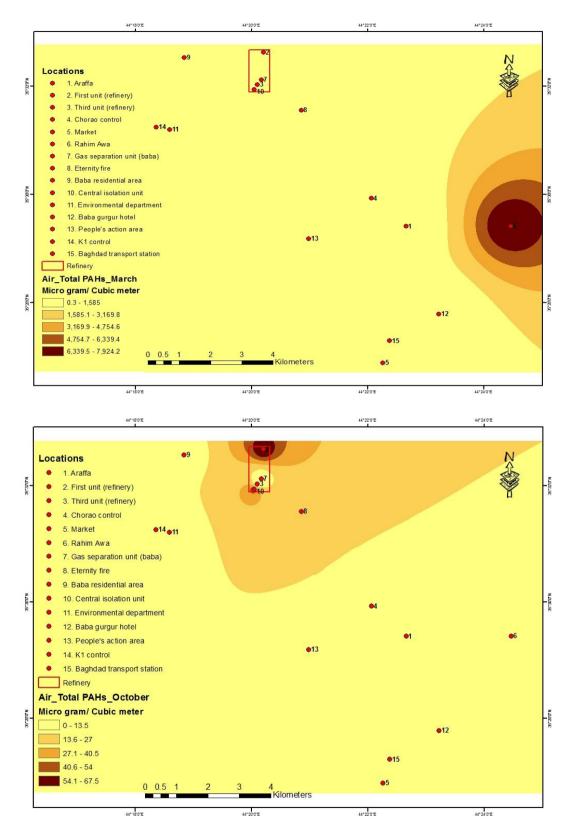


Fig.(4-11) : GIS Map showing PAHs (Total) distribution in air of the studied area in october 2010 and march 2011 .

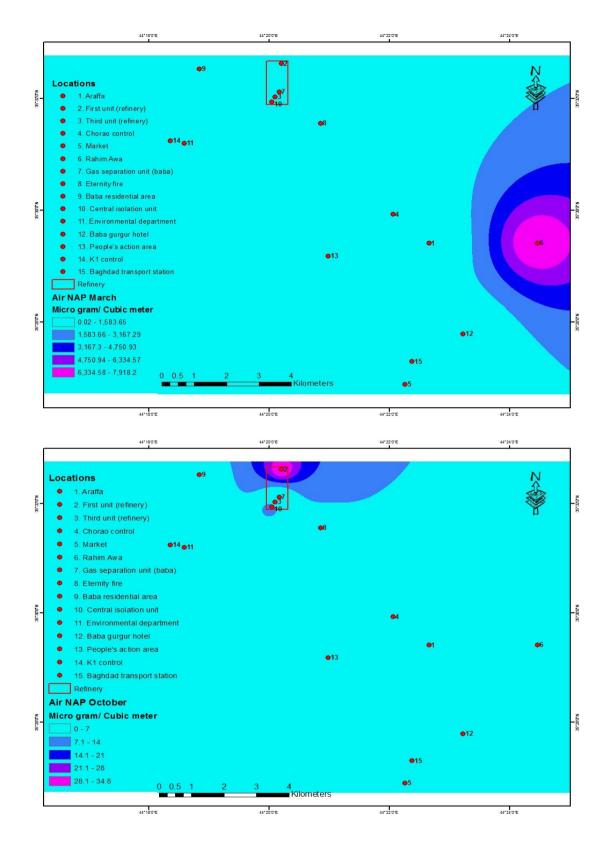


Fig. (4-12): GIS Map showing Naphthalene distribution in air of the studied area in October 2010 and March 2011.

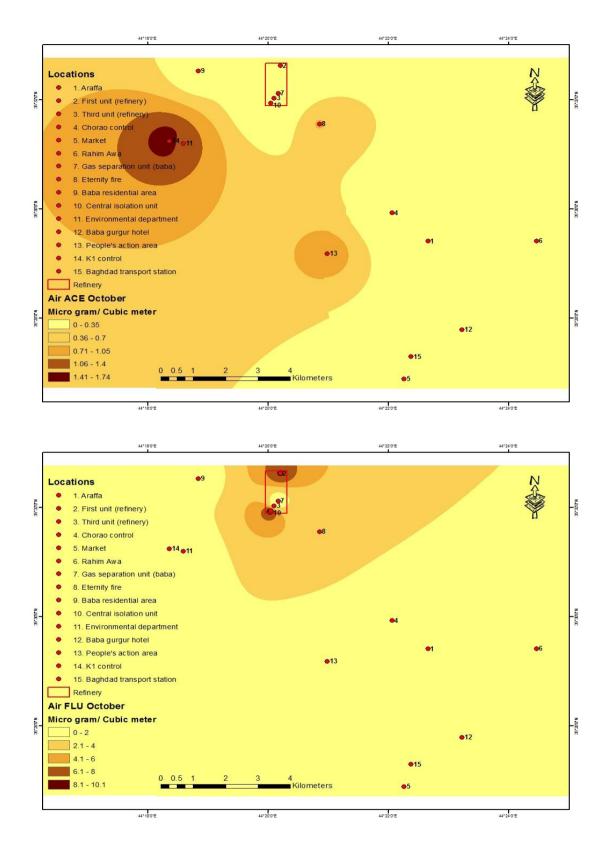


Fig.(4-13) : GIS Map showing Acenephthen and Fluorine distribution in air of the studied area in October 2010

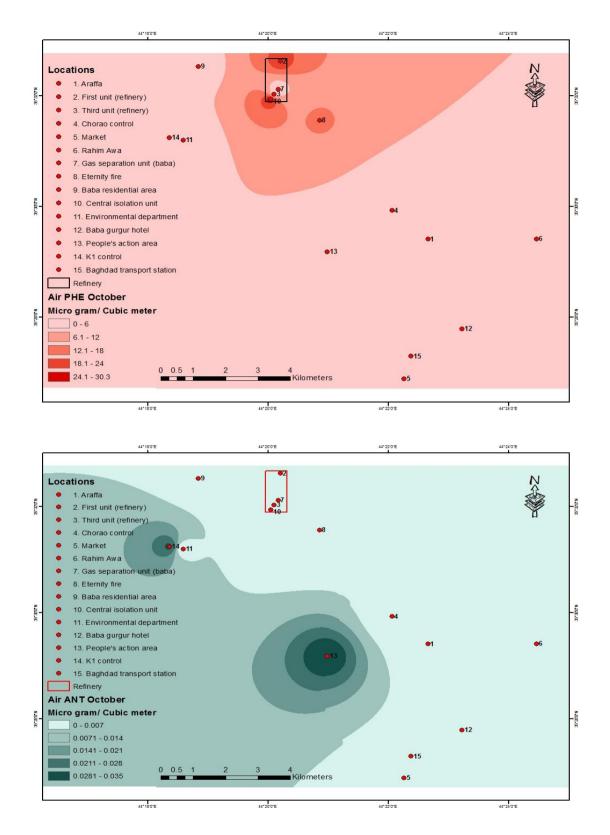


Fig. (4-14): GIS Map showing Phenanthren and Anthracene distribution in air of the studied area in October 2010.

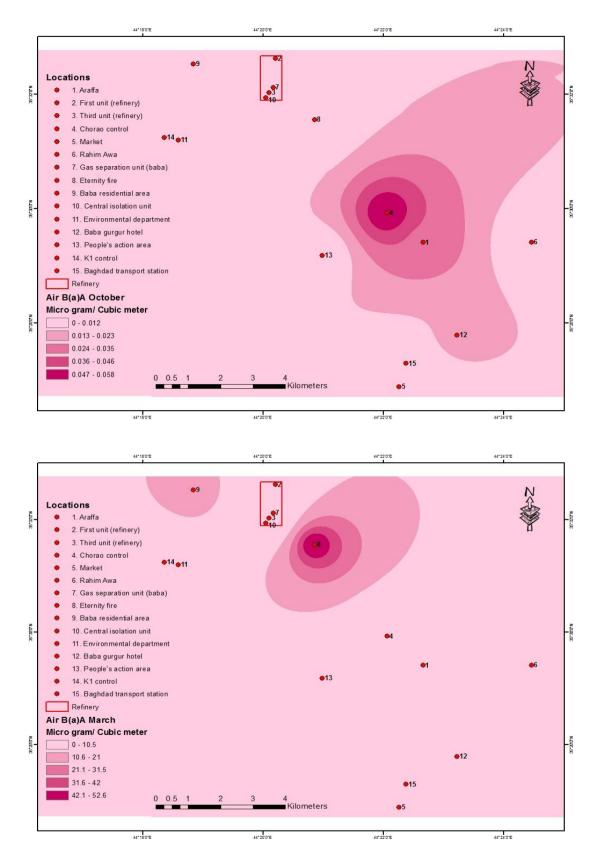


Fig. (4-15): GIS Map showing Benzo (a) Anthracene distribution in air of the studied area in October 2010 and March 2011.

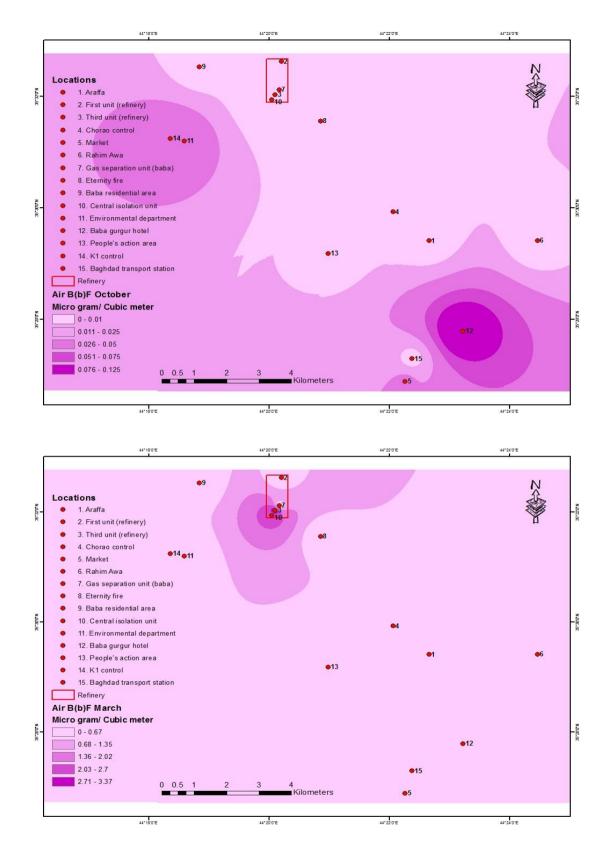
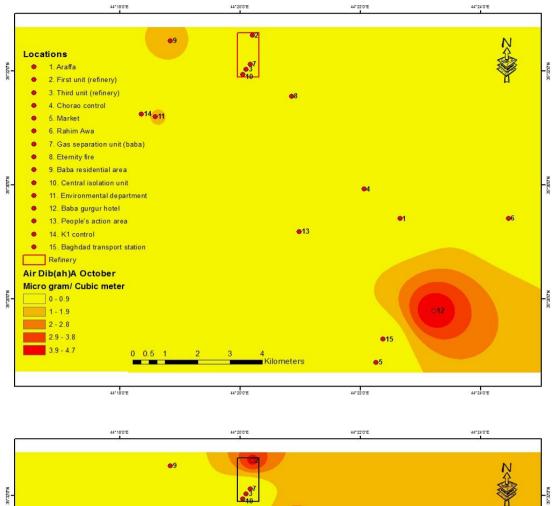


Fig. (4-16): GIS Map showing Benzo (b) fluranthene distribution in air of the studied area in October 2010 and March 2011.



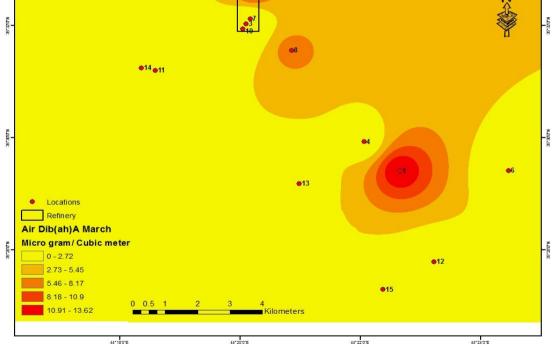


Fig. (4-17): GIS Map showing Dib (ah) Anthracene distribution in air of the studied area in October 2010 and March 2011.

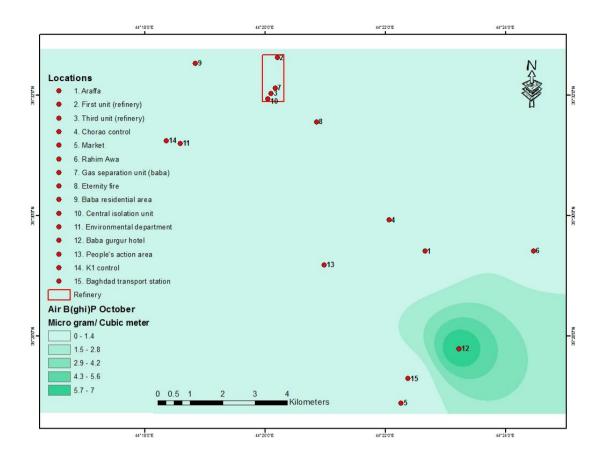


Fig. (4-18): GIS Map showing Benzo (ghi) perylene distribution in air of the studied area in October 2010.

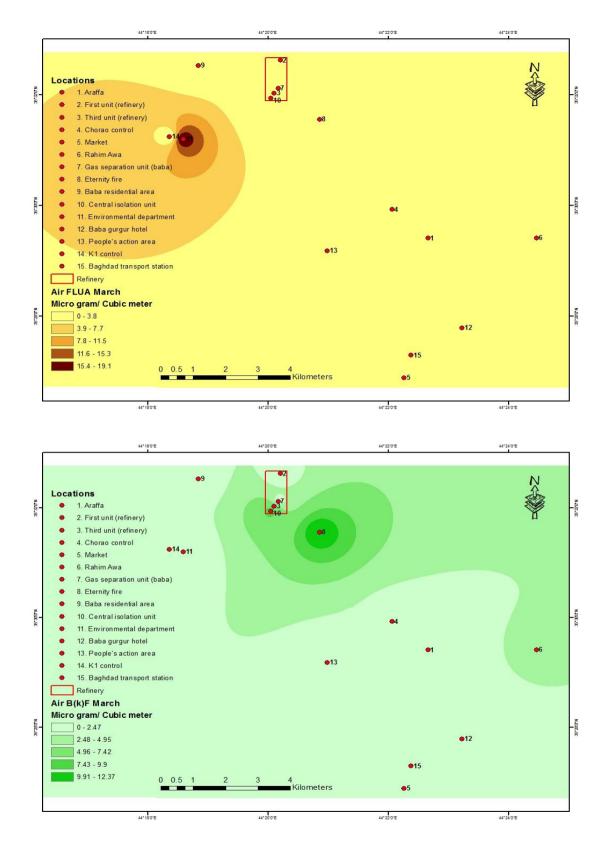


Fig. (4-19): GIS Map showing Fluranthene and Benzo (k) Fluranthene distribution in air of the studied area in March 2011.

4.2. Soil pollution

There are many types of soil pollution and one of which is caused by heavy metals, such as Cadmium, Lead, Chromium, and Copper, etc and can be a serious problem if present in soils at high concentrations. Although heavy metals are naturally present in soil, contamination may come from local sources: mostly industry (mainly non-ferrous industries, but also power plants effluents , iron & steel industries , chemical industries, aggregation activities (irrigation with polluted waters, sewage sludge and fertilizer, especially phosphates, contaminated manure and pesticide containing heavy metals), waste incineration, combustion of fossil fuels and road traffic all can cause different types of heavy metals partials to be spread to the environment we live in (Onder et al 2007).

Heavy metals can be found generally at trace levels in soil and vegetation, and living organisms may need the micro-elements of these metals. (Onder et al 2007).

Some of the main soil pollutant elements are studied in this research and an illustration to those studies and findings is given below.

4.2.1. Heavy metals

Heavy metals are naturally present in soil; yet contamination comes from local sources, industry, agriculture, waste incineration, combustion of fossil fuels and road traffic because they are considered as the main source of anthropogenic of heavy metals. (Asgari 2011; Suciu et al 2008)

Purely theoretically, every 1000 kg of "normal" soil contains 200 g of Chromium, 80 g Nickel, 16 g Lead, 0.5 g Mercury and 0.2 g Cadmium; therefore it is not always easy to assign a definite cause for the increment of heavy metal content. Those metals are described as "heavy metals", in their standard state. Normally heavy metals have a specific gravity (density) exceeding 5 g/cm3. Some of that are Copper, Nickel, Chromium and Iron. The presence of some concentration of heavy metals is considered essential for the survival of all forms of life. These are described as essential trace elements (Caobisco, 1996).

Heavy metal is one type of pollutants that has a big potential harm to ecological environment because they cannot be biodegraded when releasing into environment. (Li et al 2010).

The heavy metals present in soil that was investigated around the study area of this research are described below.

4.2.1.1. Lead (Pb)

The average concentration of Lead (Pb) that was found in the soils of the studied area during October 2010 was 5.687ppm. The maximum value recorded was 15.0ppm at site no.14 (K1 control) and the minimum value was 0.5ppm at site no.6 (Rahim Awa site). These results changed during March 2011 when the average was 14.267ppm with a maximum value of 30.0ppm at site no.9 (Baba Residential Area site) and a minimum value of 0.65ppm at site no.6 (RahimAwa site). Comparison with the world average the concentrations of Pb were lower during the two periods of measurements as seen in (table 4-9, 10). The increment of Pb between the two periods belong to the increasing operations of oil production at the refinery.

4.2.1.2. Copper (Cu)

Copper concentrations was found to have an average of 8.06ppm and 5.30ppm during October 2010 and March 2011 respectively which is lower than the world allowable averages (20ppm) these findings can be seen in (tables 4-9, 10).

From the table it is seen that in October the maximum value obtained was 15.0ppm at site no.10 (Central Isolation Unit), and the minimum value was 3.0ppm at site no.8 (Eternity fire site). Moreover the maximum value of Copper during March was 28.88ppm at site no.10 (Central Isolation Unit) and the minimum value was 0.05 at site no.11 (The Environmental Department site) for the same month.

The difference between the two periods in averages reflects the effects of the meteorological changes. The increasing of Cu concentration at some sites was due to the increment of the fuel combustion operations which occurred during March.

4.2.1.3. Nickel (Ni)

Nickel concentrations in soils were also investigated on this study and they were lower than that of the world average allows. This was true for both periods of this study. Were results shows an average in October 2010 of 32.438 with a maximum value of 48 ppm at site no. 10(Central Isolation Unit) and as minimum as 11ppm at site no.12 (Baba Gurgur hotel site). Same wise the average in March 2011 was 43.95ppm and reaching as maximum as 77.27 ppm at site no.9 (Baba Residential Area) and as minimum as 0.08ppm in site no. 11 (The Environmental Department site). To explain this increment in both averages between the two periods it can be related to fuel combustion increment that occurred on March compared with that of October.

4.2.1.4. Chromium (Cr)

As a result of the increment of the combustion fuels operation at the refinery during march in addition to other factors such as parent rocks effect Chromium concentrations in soils have increased, were soil tested for Chromium concentrations showed that in October they were having an average of 56.625ppm in which a maximum value of 81ppm at site no.11 (The Environmental Department site) and a minimum value of 31ppm at site no.8 (Eternity fire site), this changed to become of an average at 65.937ppm with a maximum value of 90 ppm at site no.14 (K1 control) and a minimum value of 25 ppm at site no.10 (Central Isolation Unit) during March .

4.2.1.5. Cadmium (Cd)

The last heavy metal that was tested in the soils during this study was Cadmium; the averages recovered were 12.60ppm, 7.439ppm for October and March respectively. If this is compared with the world allowable average 5ppm then it would be clear that both values were higher. Table (4-9, 10) demonstrates those findings. From the table it is observed that the maximum value in October was 19.82ppm at site no.9 (Baba Residential Area) and the minimum value was 3.81ppm at site no.10 (Central Isolation Unit), meanwhile in March the maximum and minimum values were 11.93ppm and 3.62ppm at site no. 15(Baghdad Central Station) and at site no.2 (The First Unit of Refinery) respectively. This reduction in the concentration averages reflects the effect of meteorological conditions at the studied area.

Table (4-10): Heavy metals concentrations in soil of the studied area inOctober 2010

Sample	Pb	Cu	Ni	Cr	Cd	
No.	ppm	ppm	ppm	ppm	ppm	
1	2	10.0	44	44 60		
2	3	7.0	22	48	19.04	
3	4	5.0	15	37	15.66	
4	13	5.0	22	46	19.39	
5	2.0	6.0	23.0		7.27	
6	0.5	8.0	36	68	8.55	
7	1.0	6.0	42	60	13.35	
8	3.0	3.0	13	31	13.79	
9	11.0	8.0	40	56	19.82	
10	2.0	15.0	48	70	3.81	
11	14.0	11.0	62	81	11.16	
12	10.0	4.0	11	37	9.57	
13	2.0	10.0	46	76	10.08	
14	15.0	11.0	35	70	15.17	
15	5.0	12.0	30	68	6.29	
16	4.0	8.0	30	53	9.39	
Mean	5.719	8.06	32.438	56.625	12.60	
World limits	150	20	100	250	5	
LSD (p<0.05)	1.1025	0.3577	0.4085	0.6838	0.4565	

Sample	Pb	Cu	Ni	Cr	Cd
No.	ppm	ppm	ppm	ppm	ppm
1	24.49	9.19	72.14	80.0	9.84
2	3.16	0.1	63.92	70.0	3.62
3	17.86	0.1	0.03	70.0	4.45
4	9.4	7.43	67.92	70.0	8.48
5	6.4	5.23	65.0	60.0	6.54
6	0.8	0.1	69.88	80.0	7.40
7	0.5	0.1	26.63	70.0	7.48
8	5.03	6.31	38.92	50.0	5.69
9	49.43	26.96	77.27	70.0	9.32
10	49.93	28.88	35.25	25.0	8.16
11	39.12	0.05	0.08	60.0	6.73
12	7.6	0.1	33.57	80.0	9.33
13	0.23	0.09	70.82	60.0	5.73
14	0.8	0.1	0.09	90.0	7.25
15	8.93	0.07	66.06	60.0	11.93
16	5.33	0.09	15.64	60.0	7.08
Mean	14.313	5.30	43.95	65.937	7.439
World limits	150	20	100	250	5
LSD (p<0.05)	0.3898	0.1265	0.1444	0.2418	0.1614

Table (4-11): Heavy metals concentrations in soil of the studied area inmarch 2011.

Table (4-12) Heavy metals averages in soils of some national and world studies(modified after Salman 2007).

Country	Pb	Cu	Ni	Cr	Cd	Reference
Kirkuk	10.016	6.68	38.194	61.281	10.019	The Current Study
Baghdad	43	n.a	172	n.a	19	Habib et al 2012
Kirkuk	45	60	n.a	n.a	0.5	Mohammed 2009
Kirkuk	n.a	23-42	110-189	270-360	n.a.	Ali 2007
Basra	39.4	16.9	20.9	161.9	5.5	Salman 2007
Baghdad	153.7	91.9	111.4	n.a	5.25	Al-Maliky 2005
USA	10.1	17.3	18.3	24.1	0.16	Burt et al., 2003
Brazil	50	53	30	100	3	Deabreu et al., 2005
Hungary	18	12	25	30	n.a	Peter, 2004
World						
average	10	30	40	100	0.06	Lindsay, 1979

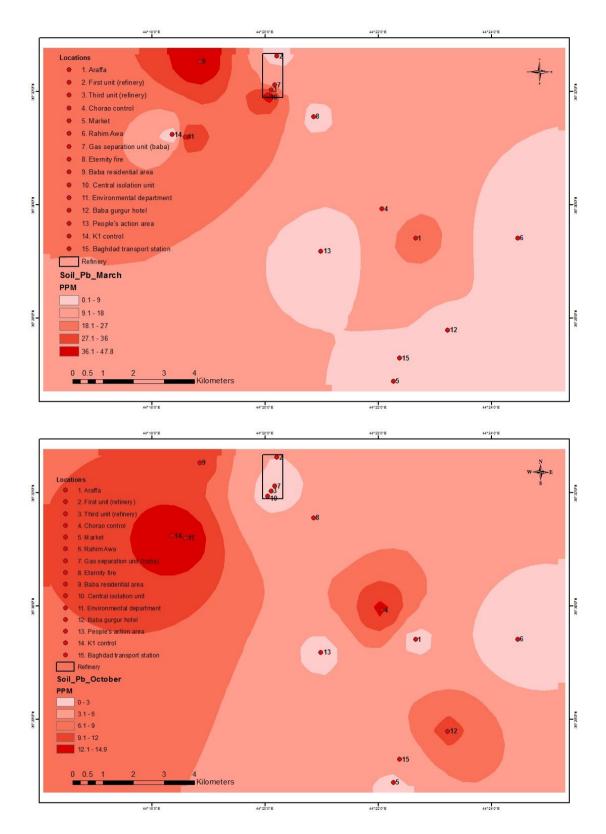
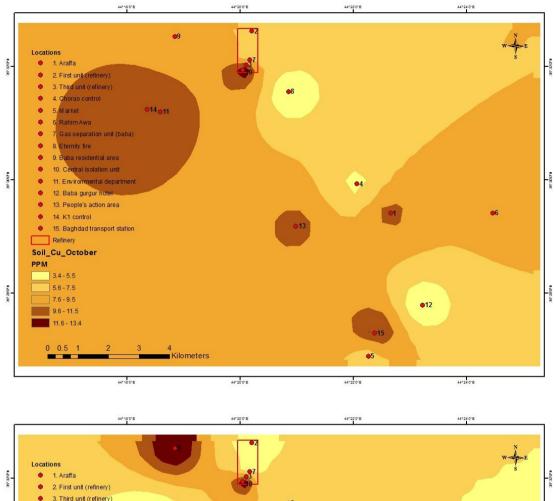


Fig.(4-20): GIS Map showing Lead (Pb) distribution in soil of the studied area in october 2010 and march 2011.



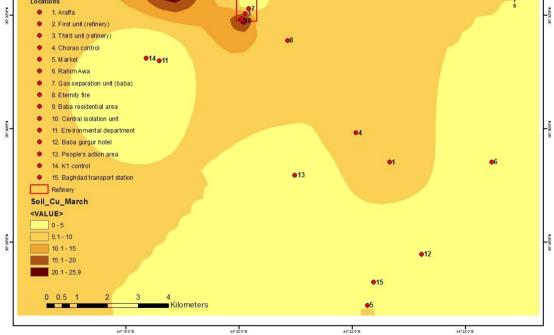


Fig. (4-21): GIS Map showing Copper distribution in soil of the studied area in October 2010 and March 2011.

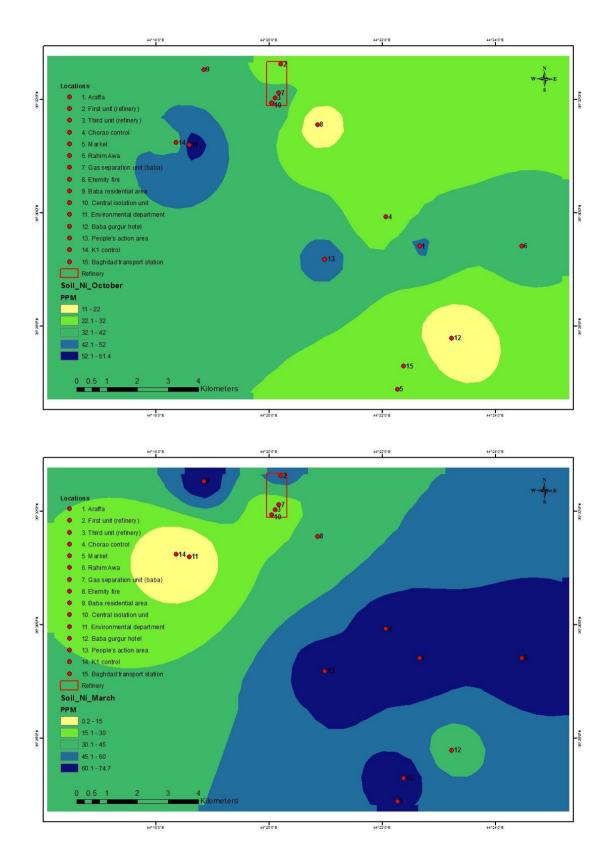
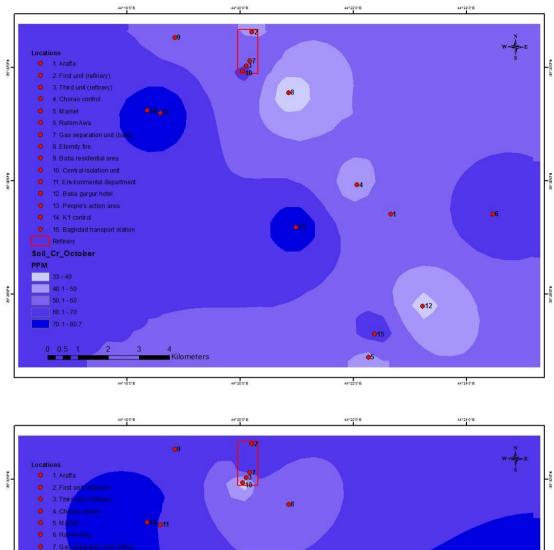


Fig. (4-22): GIS Map showing Nickel distribution in soil of the studied area in October 2010 and March 2011.



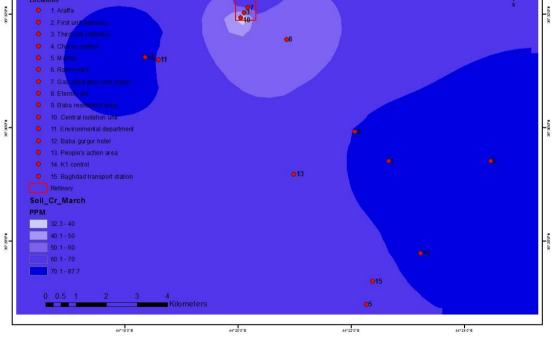


Fig.(4-23): GIS Map showing Chromium distribution in soil of the studied area in October and march 2011 .

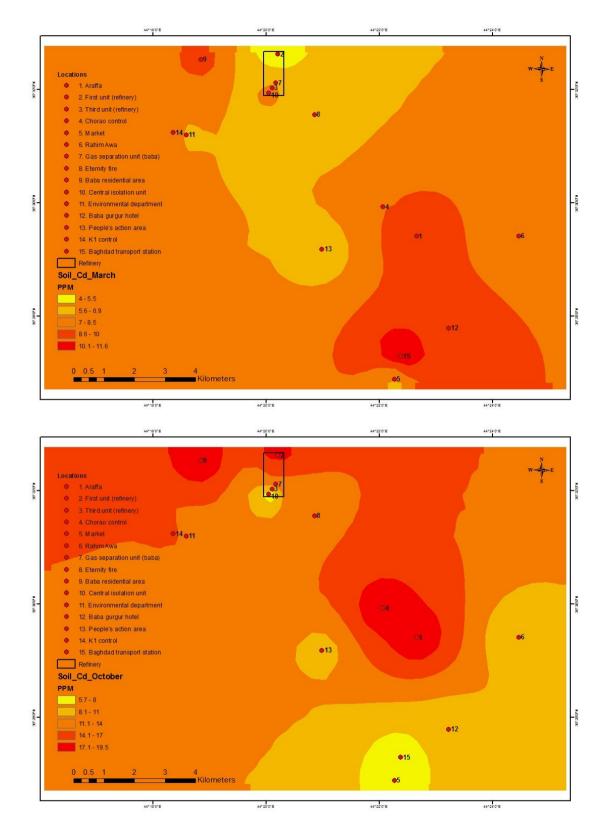


Fig. (4-24): GIS Map showing Cadmium distribution in soil of the studied area in October2010 and March2011.

4.2.2. Poly aromatic hydrocarbons

Poly aromatic hydrocarbons are represented by the form of PAH, and those substances can be found in numerous elements within the natural environment (water, soil, sediments). However, it has been proved that the main PAH compounds can sink into the soil, where they can undergo degradation depending on the environmental conditions and soil properties (Oleszczuk 2007).

PAH laden aerosols are transported from air to soil and water via physical processes which involves impaction of surfaces, gravitational settling and scavenging by rain and snow. Transfer rates are also highly sensitive to particle size (Newsletter 2003). Petroleum production can lead to contamination of soil and groundwater. (Paul et al 2006).

PAHs are relatively neutral and stable molecules; they have low solubilities and low volatilities properties, except for those small components like naphthalene. Their lipophilicity is rather high also they show long half-lives in geological media.

In aerobic sediment, for example, half lives of PAHs ranges from 3 to 300 weeks as in naphthalene and benzo[a]pyrene respectively. PAHs are regarded as persistent organic pollutants (POP) for the environment. This persistence of PAH increasing relatively with ring number and condensation degree (Henner et al 1997).

Carcinogenic PAHs are found in most surface soils. Typical concentrations in forest soil ranges from 5 μ g to 100 μ g/kg. Substantial amounts of PAHs are transferred to forest soil from vegetative litter because the compounds are adsorbed from air on organic matter such as leaves and needles. Rural soil contains carcinogenic PAHs at levels of 10–100 μ g/kg originating mainly from atmospheric fallout. For both

forest and rural soil, values as high as 1000 μ g/kg may occasionally be found (WHO 2000).

The highest concentration of PAHs that was found in the soils of the studied area in October was 285.7ppb at site no.11 (Environmental Department), meanwhile the lowest concentration of PAHs was 0.017 ppb at site no.2 (The First Unit of Refinery). Table (4-13) and fig. (4-25) shows the measurements made for PAHs concentrations.

Table (4-14) and fig (4-25) below show that highest total concentration of PAHs found in the soils of the studied in March was 69.325ppb at site no.8 (The Eternity Fire), and the lowest concentration of PAHs recorded was 0.014 ppb at site no.2 (The First Unit of Refinery).

It is also observed that the average of total concentrations of PAHs in March was (10.92ppb) which was lower than the corresponding values during October (26.92ppb). This is a result of degradation of PAHs which happened in different soils and the meteorological conditions present.

In the soil environment, the PAHs may undergo degradation related to conditions and soil properties (Oleszczuk 2007).

Figures (4-25 to 4-33) show those distributions of PAHs in the soil of the studied areas. Appendix (2) represents HPLC & GC-MS Chromatograms of PAHs in the Soil of the Studied Area at the Two Periods.

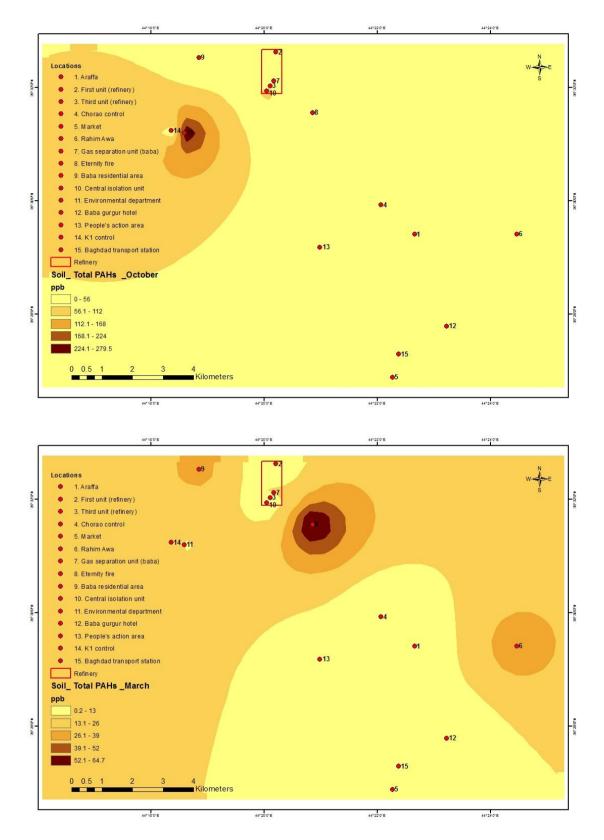


Fig. (4-25): GIS Map showing Total PAHs distribution in the soil of the studied area in October 2010 and March 2011.

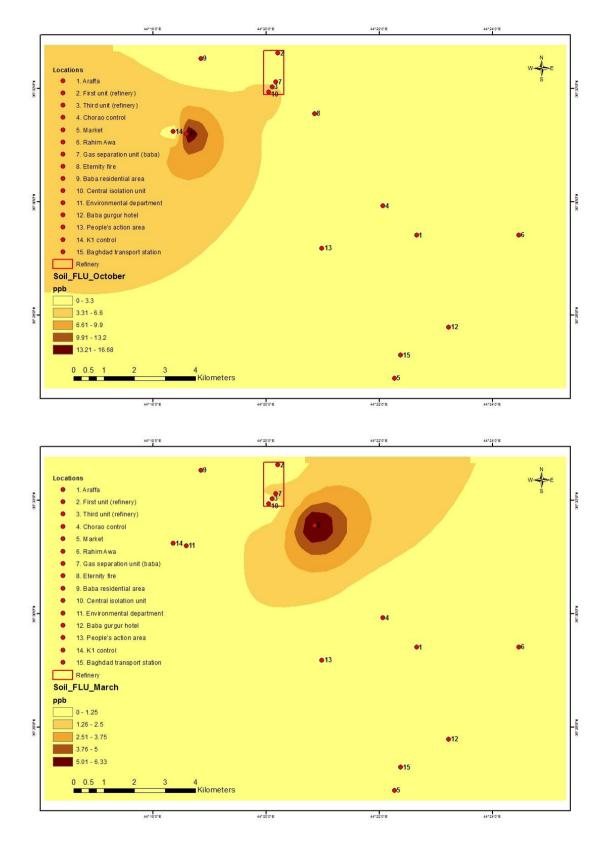


Fig. (4-26): GIS Map showing Fluorine distribution in the soil of the studied area in October 2010 and March 2011.

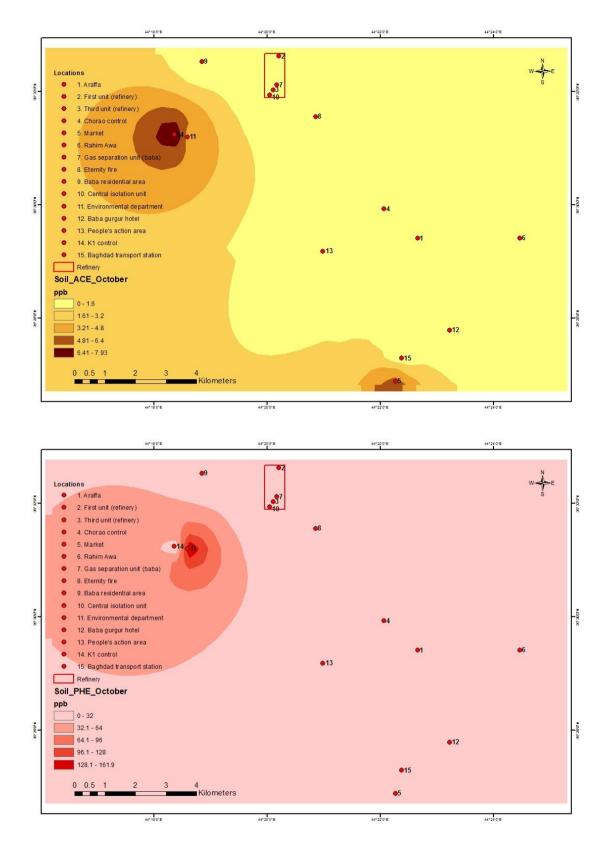


Fig. (4-27):GIS Map showing Acenephthene and Phenanthrene distribution in the soil for the studied area in October 2010.

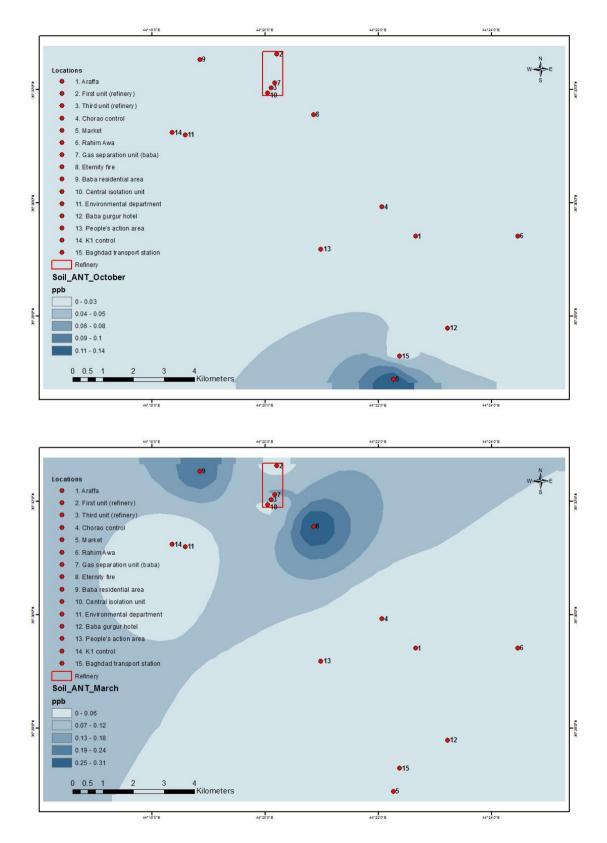


Fig. (4- 28): GIS Map showing Anthracene distribution in the soil of the studied area in October 2010 and March 2011.

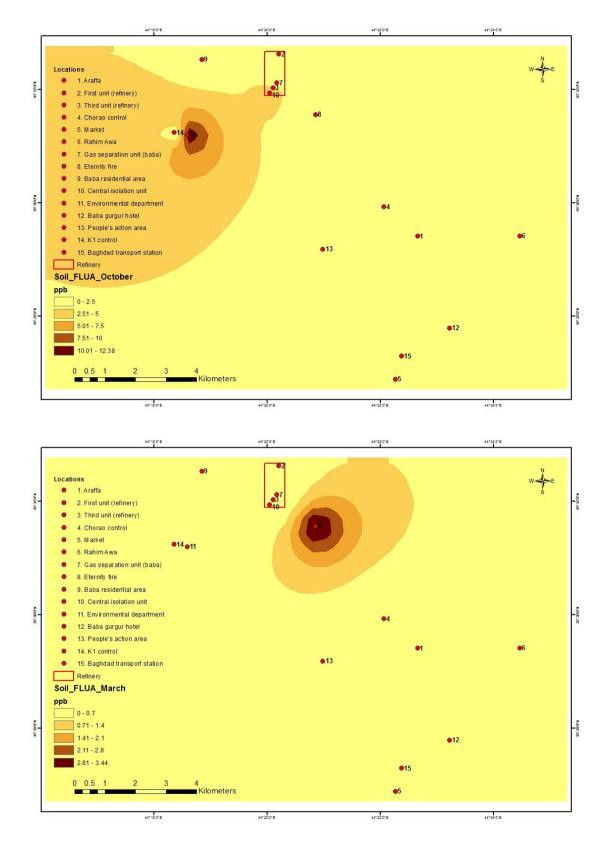


Fig. (4-29): GIS Map showing Fluoranthene distribution in the soil of the studied area in October 2010 and March 2011.

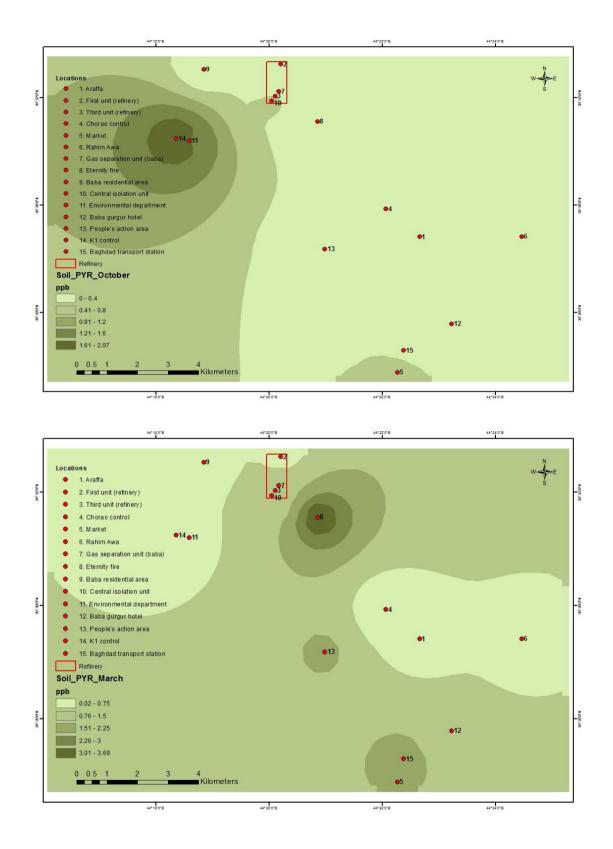


Fig. (4-30): GIS Map showing Pyrene distribution in the soil of the studied area in October 2010 and March 2011.

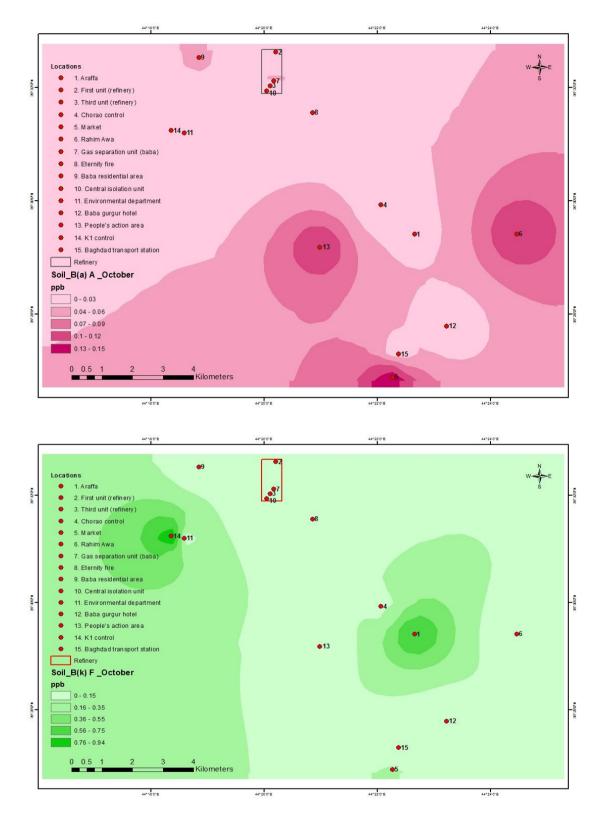


Fig. (4-31): GIS Map showing Benzo(a)Anthracene and Benzo(k)Fluoranthene distribution in the soil of the studied area in October 2010 .

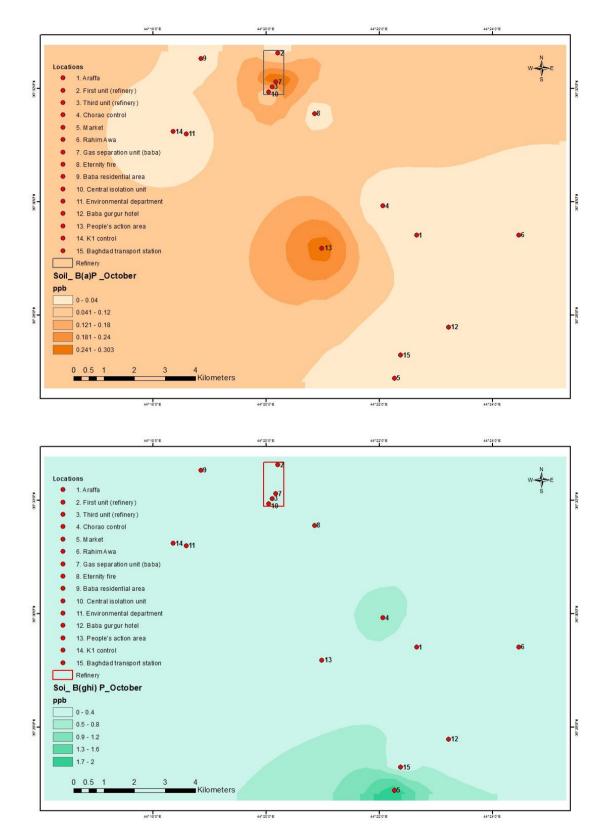
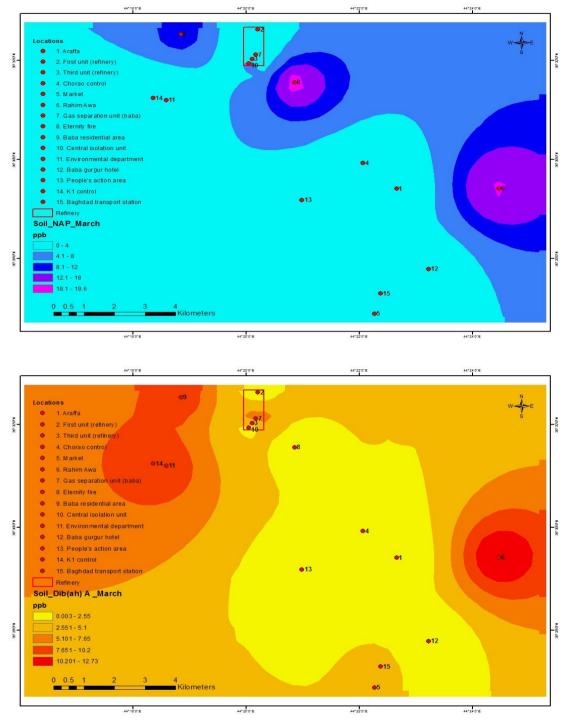


Fig.(4-32): GIS Map showing Benzo (a) Pyrene and Benzo (ghi) Perelyne distribution in the soil of the studied area in October 2010





Dibenzo(ah)Anthracene distribution in the soil of the studied area in March 2011.

4.3. Plant pollution

Determination of chemical composition of plants is one of the most frequently used methods of monitoring environmental pollution. Various plants have been used as bioindicators to assess the impact of a pollution source on the vicinity which is due to high metal accumulation of plants (Lawal et al 2011).

Plants are the main essential parts of ecosystem, and attention to their sensitivity to air pollution is more important than standards of air pollution (Assadi et al 2011).

Responses of trees to air pollutants may vary widely and these variations can be caused by many factors, such as differences in pollutant concentrations and distribution in time, the genetic origin, physiological activity and nutritional status of plants as well as effects of various environmental factors. (Assadi et al 2011).

Eucalyptus globules is one of the most commonly grown forest tree species in Australia, Portugal and other subtropical and Mediterranean areas. Its high growth rate makes it ideal as a plantation species because the rate of wood production from intensively managed plantations greatly exceeds that of native forests. *Eucalyptus globulus* is also valued as an ornamental tree in urban areas, and it is the dominant genus in many natural types of woodland, these species attain heights ranging between 25 and 35 m (Pearson 1995). Plant leaf is the most sensitive part to be affected by air pollutants as major physiological processes are concentrated in the leaf (Naveed et al 2010).

From the above illustration it became essential to study and examine plant leaves to evaluate air pollution concentrations in the study area, that is because leaves are considered to be the most vital part of tress that detect pollution as it is in direct contact with the surrounding atmosphere.

Elements in plant leaves (heavy metals, Polycyclic aromatic hydrocarbons), were investigated to evaluate the pollution in the study area .Those investigation and findings are illustrated in below.

4.3.1. Heavy metals

As already mentioned previously heavy metals are considered important constituents of pollutants. They are non-biodegradable; hence these are not readily detoxified and removed by metabolic activities once they are available in the environment. This may subsequently lead to their gradual build up to toxic levels or bioaccumulation in the ecosystem (Lawal et al 2011) .Plants and animals also take up small amounts of contaminant heavy metal compounds and can concentrate them in various locations (Caobisco 1996). The high concentration of heavy metals in soils is eventually reflected by higher concentrations of metals in plants (Buszewski, 2000).

The main heavy metals that were measured and tested in plants during this study can be seen in the paragraphs below; from which a full and clear pollution analysis and assessment is then made to the studied area .

4.3.1.1. Lead (Pb)

The concentration of Pb that is considered toxic in plants lies in the range of 30 to 400 μ g/g (Naveed et al 2010). The average of Lead in leaves of Eucalyptus taken from the studied area in October recorded a value of 3.439 ppm, also figures as high as 10.0 ppm at site no.5 (The

Market site) and as low as 0.2 ppm at site no.11(The Environmental Department site) were plotted .

Same wise Lead concentrations in leaves were measured in March and was found to have an average of 1.39 ppm and a highest value of 4.0ppm at site no.5 (The Market site) and lowest value of 0.01 ppm at site no.11 (The Environmental Department site).

This noticed decrease in the concentration of Lead in Eucalyptus leaves from October to March is related to its concentration in air at the same period which may be referred to the meteorological elements which occur during different seasons.

4.3.1.2. Copper (Cu)

The average of Copper in the leaves of Eucalyptus of the studied area in October was found to be 4.064 ppm with a high value of 10.0 ppm at site no.11 (The Environmental Department site) and low value of 0.02 ppm at site no.1 (Araffa site). This changed to be an average Copper concentration in March 3.03 ppm with a high value of 10.3ppm at site no.6 (RahimAwa site) and a low value of 0.008 ppm at site no.11 (The Environmental Department site). Again this noticed Decrement in the concentration of Copper in Eucalyptus leaves between the two periods can be related to the effect of meteorological elements.

4.3.1.3. Nickel (Ni)

Nickel concentrations found on Eucalyptus leaves taken from the study area in October was 6.06 ppm and the highest value was 18.0 ppm at site no. 11 (The Environmental Department site) and the lowest value was 1.0 ppm at site no.13 (The Peoples Action Area), These results changed in March to have an average value of 37.66 ppm with a

high reading of 54.82 ppm at site no.8 (The Eternity Fire) and low reading of 16.26 ppm at site no.10 (The Central Isolation Unit).

To explain the increment that was found between the two averages, we should link it with the fuel combustion operations of the refinery and the oil fields near the studied area, as this production increased between the two periods of the study which eventually reflected back on the pollutants concentrations in the nearby atmosphere. Again this conclusion can support itself if compared with the concentration found earlier in the soil at the same period.

4.3.1.4. Chromium (Cr)

Concentrations of (Cr) in Eucalyptus leaves in plants present in the studied area was measured and it was found to have an average during October measurements of 54.20 ppm and reaching as high as 104.49 ppm at sites no. 7(Gas Isolation Unit Baba)and at site no . 8(The Eternity Fire) and as low as of 0.01 ppm at site no. 2(The First Unit of Refinery). These results changed in March to record an average value of 46.27 ppm and a high value of 88.35 ppm at site no.8 (The Eternity Fire) and a low value of 20.66 at site no.3 (The Third Unit of Refinery).

Meteorological condition effects especially rainfall, wind speed and direction which was observed had a great role in the difference of averages that was obtained between the two periods. The other dominating factor that effected on the results obtained was the distribution of heavy metals which differed at sites of the studied areas.

4.3.1.5. Cadmium (Cd)

Cd is well known to be easily taken up by plants and transported to different organs although it had no beneficial effects to plants and animals (Yap et al 2009).

The concentration of (Cd) in Eucalyptus leaves of the studied area was investigated and was found to be at an average of 11.97 ppm during October samples. Also the highest value was 17.47 ppm at site no.2 (the first unit of the refinery) and the lowest value was 4.31 ppm at site no. 3(the third unit of the refinery) during this month. but when compared with March sample readings (average 6.6 ppm), highest value of 10.49 ppm at site no.12 (Baba Gurgur Hotel) and lowest value of 3.63 at site no.15 (Baghdad Central Station) it becomes clearly obvious that during the two periods notice there was an effect caused by the meteorological changes on the concentration of (Cd) in plant of the studied area.

Comulo	Dh	Cu	Ni	Cr	Cd
Sample	Pb	Cu	INI	Cr	Cu
No.	ppm	ppm	ppm	ppm	ppm
1	3.0	0.02	5.0	51.71	14.03
2	3.0	2.0	8.0	0.01	17.47
3	2.0	5.0	4.0	30.82	4.31
4	7.0	8.0	16.0	46.21	8.24
5	10.0	1.0	4.0	82.50	11.55
6	2.0	3.0	4.0	48.96	13.92
7	3.0	3.0	6.0	104.49	15.72
8	2.0	4.0	3.0	104.49	5.87
9	1.0	5.0	2.0	35.22	8.12
10	6.0	4.0	8.0	50.06	12.33
11	0.2	10.0	18.0	47.86	15.14
12	5.0	6.0	8.0	79.20	17.78
13	3.0	1.0	1.0	48.96	6.79
14	1.0	7.0	3.0	58.31	11.32
15	5.0	4.0	4.0	56.11	13.58
16	2.0	2.0	3.0	22.30	15.34
Mean	3.439	4.064	6.06	54.20	11.97
World allowable	3-0.05				
standard limits	ppm				
LSD (p<0.05)	0. 4375	0.3285	·.6162	0.2063	·.2499

Table (4-15): Heavy metals concentrations in leaves of plants(Eucalyptus) in October 2010.

Sample Pb Cu Ni Cr Cd No. ppm ppm ppm ppm ppm 1 0.1 3.81 36.96 40.5 9.12 2 1.2 3.2 32.22 22.3 4.66 3 0.9 4.42 45.49 20.66 7.35 4 42.52 42.36 7.52 3.2 7.66 5 4.0 2.66 22.7 47.86 3.66 6 1.2 10.3 34.36 36.55 4.96 7 1.8 0.01 33.89 82.56 7.14 8 0.8 54.82 88.35 6.31 1.98 9 0.55 0.02 43.05 30.62 7.06 10 1.9 48.22 0.01 16.26 5.42 11 0.008 41.82 44.32 0.01 5.16 12 2.4 4.44 43.14 ٦٨,٢٤ 10.49 13 42.2 40.73 1.3 3.51 8.94 14 2.56 36.91 56.22 8.21 1.6 15 0.9 1.63 39.01 50.16 3.63 16 0.4 2.3 37.26 20.68 5.97 Mean 1.39 3.03 37.66 46.27 6.6 World allowable 3-0.05 ppm standard limits LSD (p<0.05) 0.1547 0.1161 0.2179 0.0884 0.5834

Table (4-16): Heavy metals concentrations in leaves of plants(Eucalyptus) in March 2011.

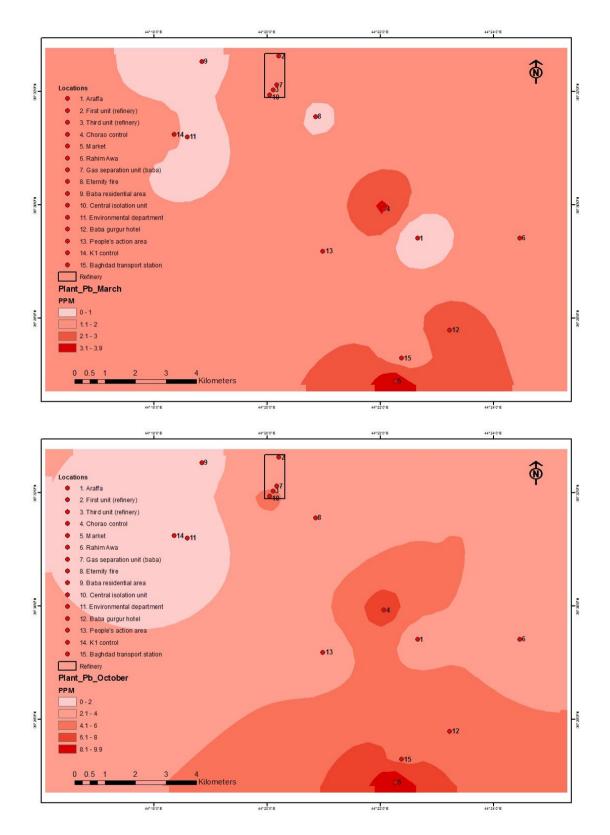


Fig.(4-34): Pb distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011 .

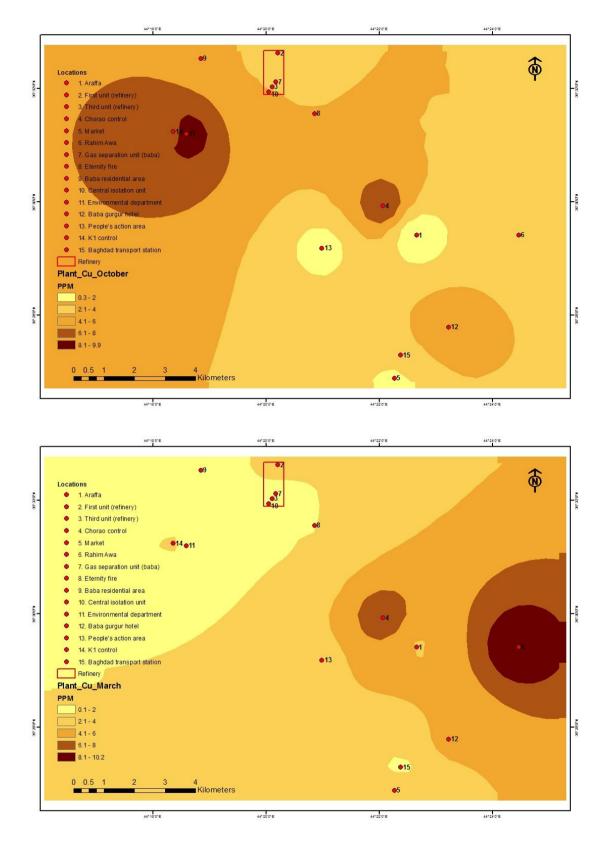
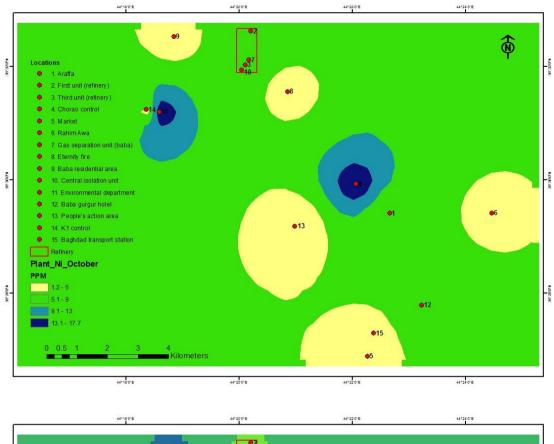


Fig. (4-35): Cu distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011 .



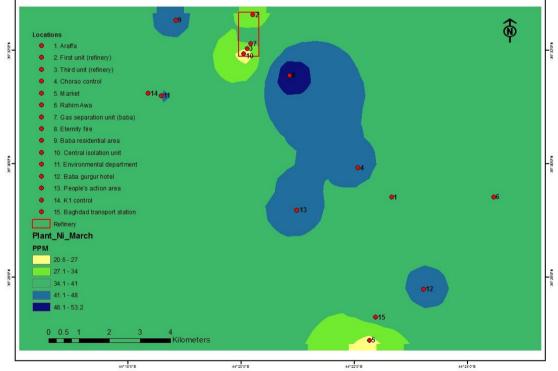


Fig. (4-36): Ni distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011.

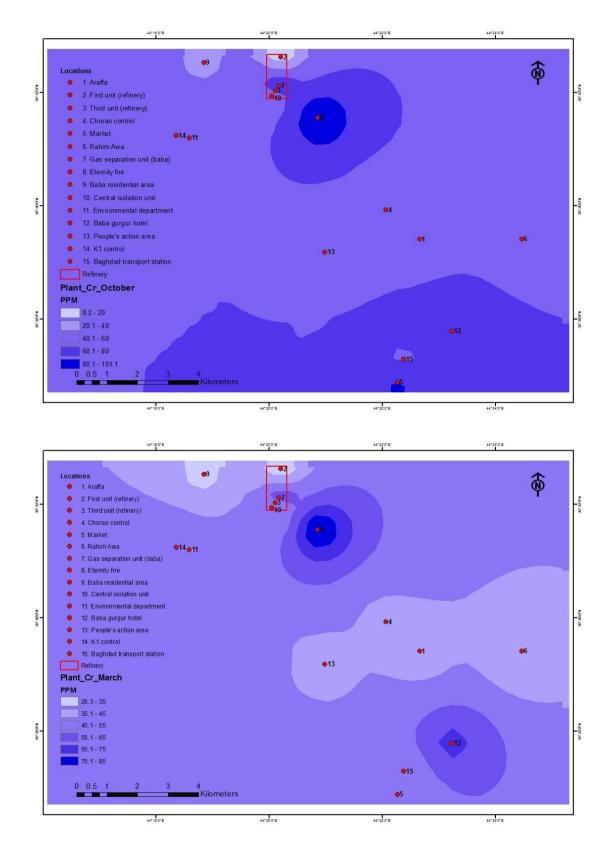


Fig. (4-37): Cr distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011.

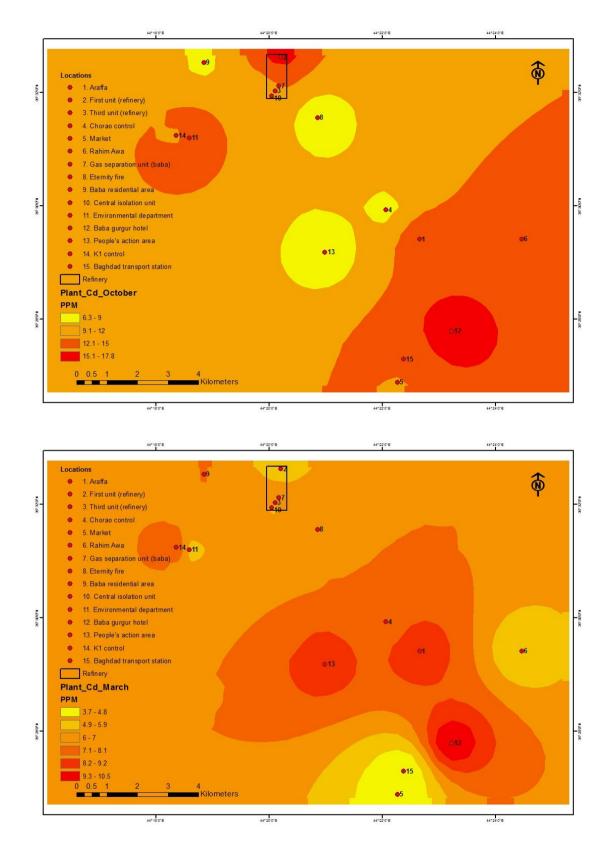


Fig. (4-38): Cd distribution in Eucalyptus leaves taken from the studied area in October 2010 and March 2011.

4.3.2. Polycyclic aromatic hydrocarbons

Since PAHs have lipophilic properties, they tend to associate with organic matter containing fatty acids and waxes. Typically, when a variety of different PAHs occur together, their overall properties will affect the environment. This effect varies according to the combination of PAHs compounds involved. Plants are important sinks for atmospheric PAHs, playing a role in the annual cycling of PAHs. Vegetation has been successfully used as a quantitative indicator of exposure to both gaseous and solid phase PAHs in ambient air (Jan et al, 2000).Due to ability of plants to accumulate organic pollutants, negative effect of plants containing such pollutants on organisms must be carefully considered (Zitka et al 2012).

Numerous studies have shown that leaves are the main sinks of airborne PAHs compounds in plants, while uptake of PAHs from soils via the root system appears to be negligible.

Because PAHs are present in both air and soil one has to consider the possible pathways of entry into plants. There are two possible pathways through which airborne PAHs can enter plants:

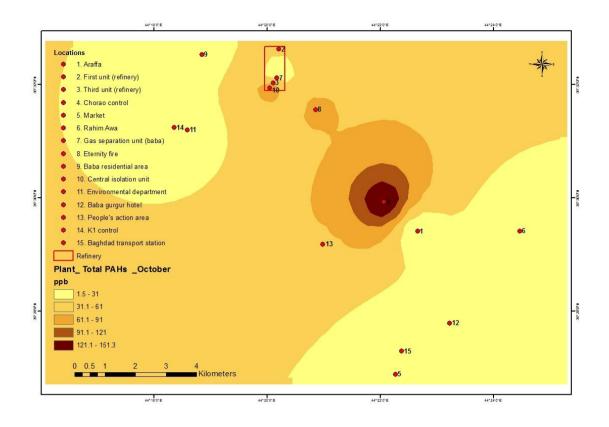
1. Uptake by root systems, once pollutants are deposited to the soil, and 2. Uptake by above-ground organs, mainly leaves, directly from air (Jan et al, 2000).

The ability of some plants to stimulate the process of the degradation of organic pollutants is applied in the techniques of phytoremediation (Oleszczuk 2007).

Trace levels of polycyclic aromatic hydrocarbons (PAHs) are widely occurring in modern ecosystems. Since some PAH members are mutagenic, their presence in plant is of an increasing concern because PAHs may ultimately be transferred to food. A recent investigation suggests that PAHs should be partitioned between air and plant as a function of ambient temperature (Bryselbout, C.et al 2000). PAHs are highly toxic to plants as well as for animals when it is present in the form of both acute and chronic intoxication depending on time of exposure and concentration of PAHs (Zitka et al 2012).

The tests carried out in this study showed a high concentration of PAHs as a total in plant leaves during October which was as high as 153.1ppb at site no.4 (Chorao Control), and as the low as 0.987 ppb at site no.6 (Rahim Awa area). Table (4-16) and fig. (4-39) show those results . To explain this we need to consider that at high ambient temperatures during summer, low molecular weight compounds can revolatilize to this atmosphere (Jan et al, 2000).

In March the maximum concentration of PAHs as a total in plant leaves taken from the studied area was found to be 298. 5ppb at site no.10 (Central Isolation Unit), with a minimum recorded value of 15.27 ppb at site no.14 (K1 Control), (table 4-17 and fig. 4-39). From those charts it is seen that the average of total concentrations of PAHs in March was (67.41ppb) which was higher than their values during October (40.34ppb). This is due to air temperatures decrease during the fall and winter season ; evergreen plants scavenge the majority of emitted PAHs(Jan et al,2000).Appendix (3) represent HPLC & GC-MS Chromatograms of PAHs in the Plant of the Studied Area at the Two Periods.



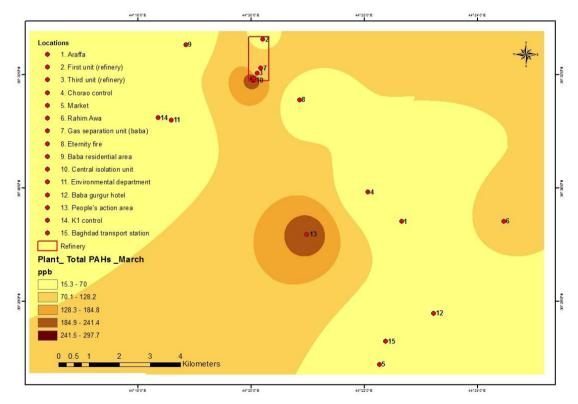


Fig. (4-39): GIS Map showing Total PAHs distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011.

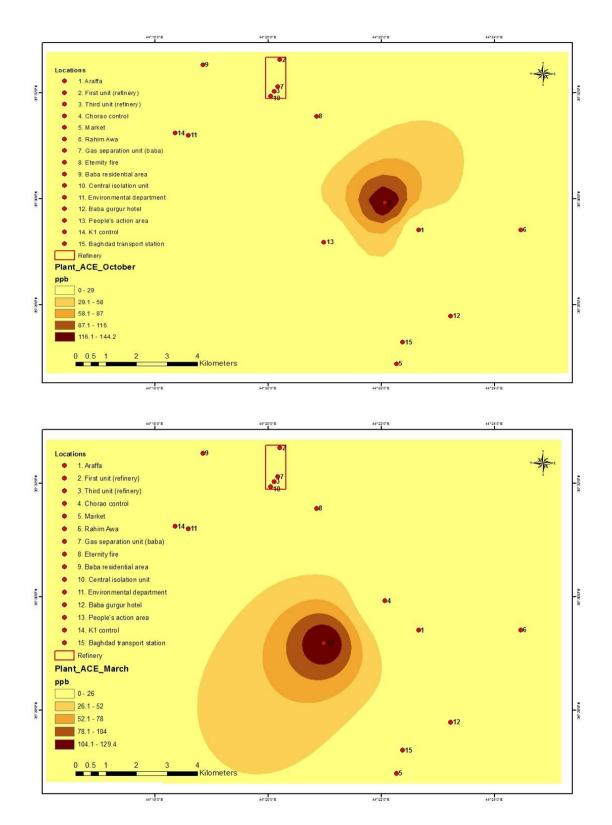


Fig. (4-40): GIS Map showing Acenephthene distribution in Eucalyptus leaves of the studied area in October 2010 and March

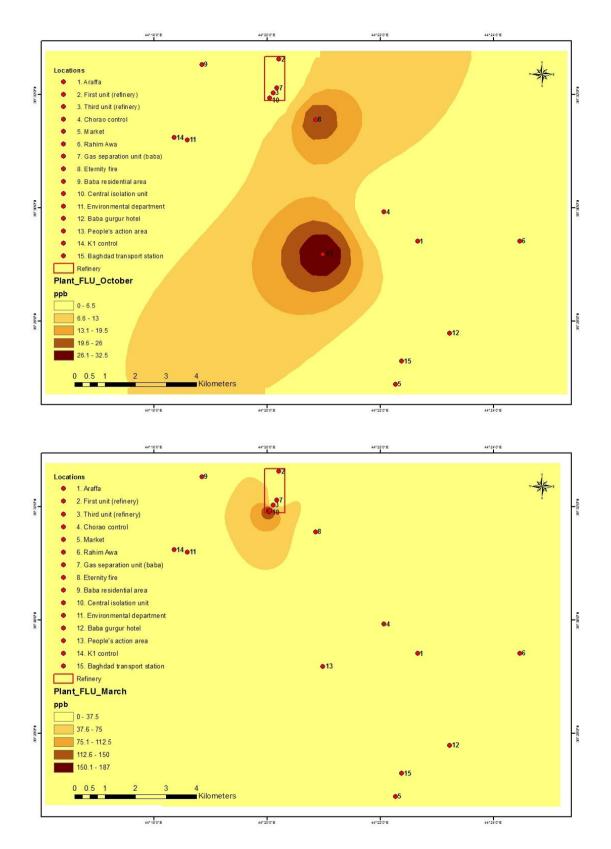


Fig. (4-41): GIS Map showing Fluorene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011.

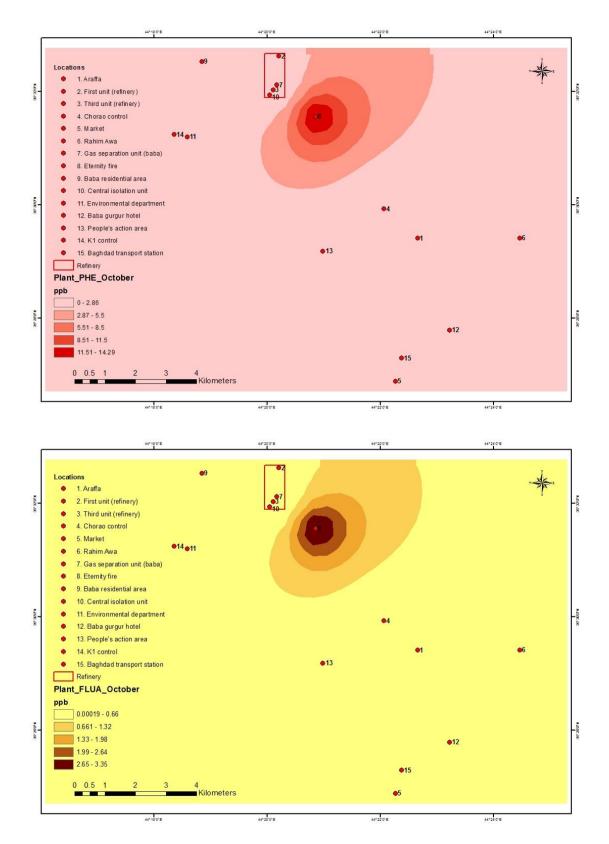


Fig. (4-42): GIS Map showing Phenanthrene and Fluoranthene distribution in Eucalyptus leaves of the studied area in October 2010

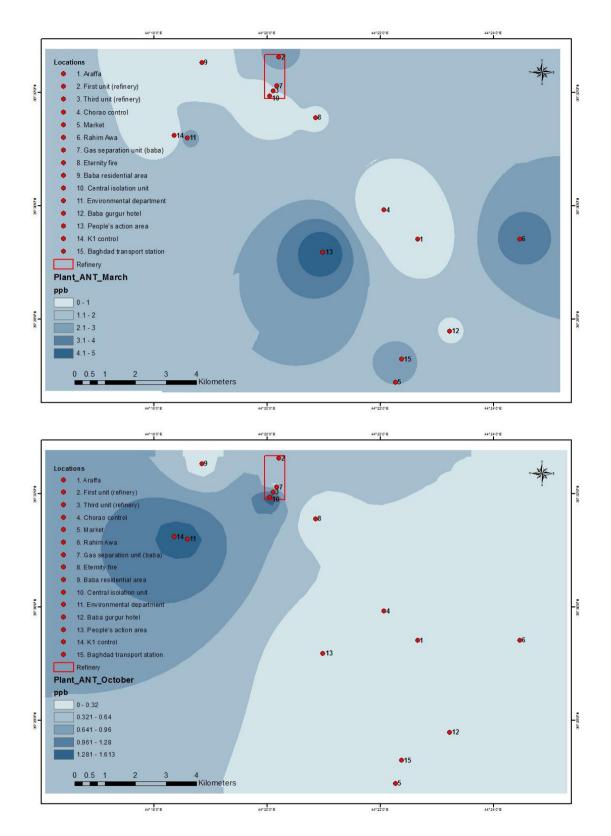


Fig. (4-43): GIS Map showing Anthracene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011.

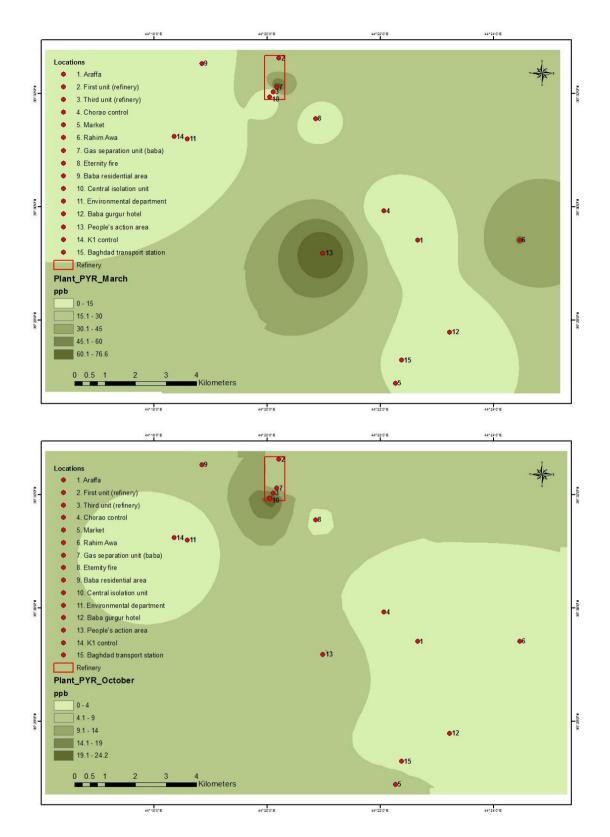


Fig. (4-44): GIS Map showing Pyrene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011.

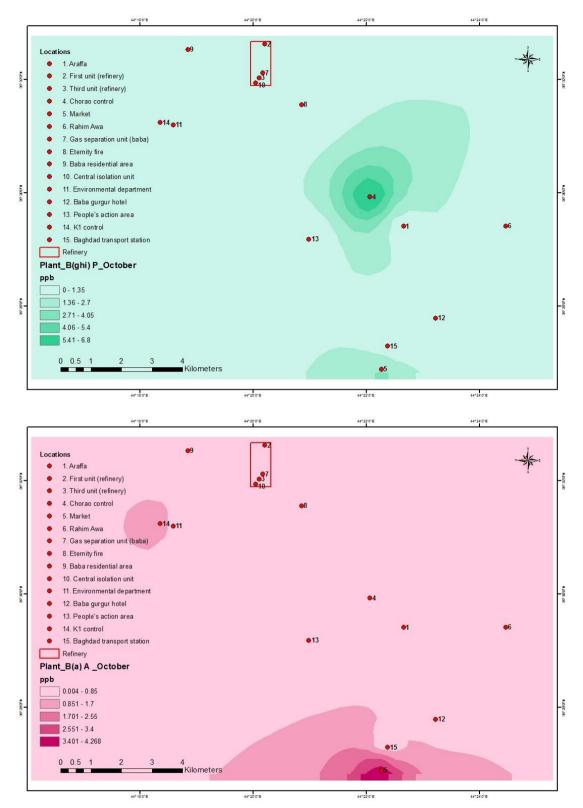


Fig. (4-45): GIS Map showing Benzo(a)Anthracene and Benzo(ghi)Perelyne distribution in Eucalyptus leaves of the studied area in October 2010 .

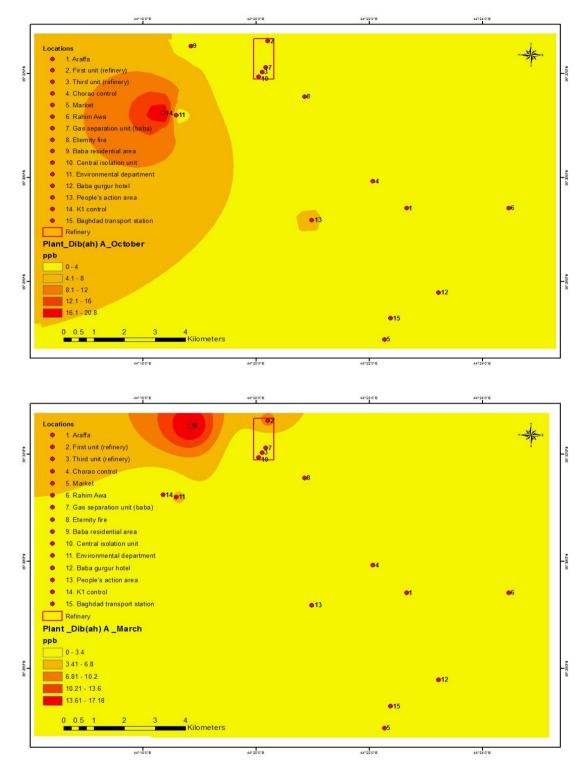


Fig. (4-46): GIS Map showing Dibenzo(ah)Anthracene distribution in Eucalyptus leaves of the studied area in October 2010 and March 2011.

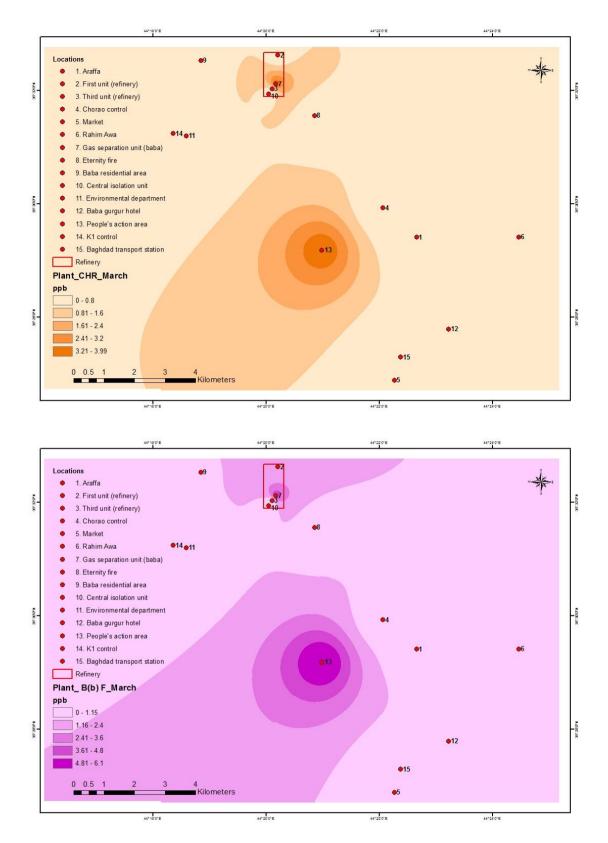


Fig. (4-47): GIS Map showing Chrysine and Benzo(b)Fluoranthene distribution in Eucalyptus leaves of the studied area in March 2011.

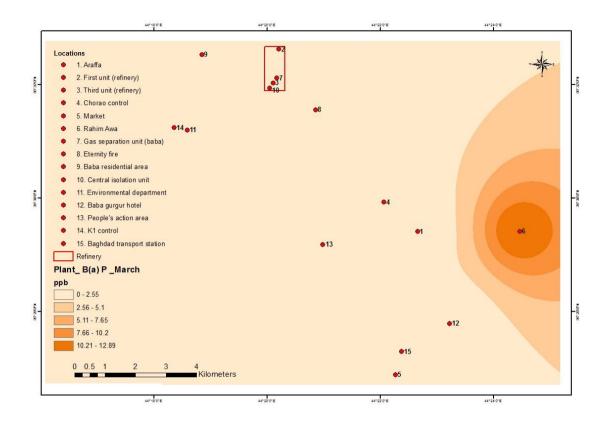


Fig. (4-48): GIS Map showing B(a)Pyrene distribution in Eucalyptus leaves of the studied area in March 2011.

Chapter Five

Modeling

5.1. Introduction

Particulate and gaseous emission of pollutant coming from industries and auto-exhaust are responsible for various environmental defaults such as rising discomfort, increasing airway diseases, decreasing productivity as well as for the deterioration of artistic and cultural patrimony in urban centers.

The continual urbanization and the emergence of megacities are prompting the need for the study of the interaction between urban activities and atmospheric chemistry (Kawabata and Ferreira 2003).

The increasing use of fuels from oil and natural gas in various fields of life lead to the spread of many air pollutants in the environment in which we live in such as gases, heavy metals and polycyclic aromatic hydrocarbons resulting from industrial activities or different modes of transport (Hashim and Sultan 2010).

The physical and chemical processes occurring in the environment all around the world are incredibly complex and scientists have only recently begun to understand and describe these phenomena's to a certain significant degree. (Bruegge 1994).

Different models are used to predict how pollutants are transported in the atmosphere from the source point of the pollutant release to a certain distant where a receptor at a certain location receives it; the pollutant concentration at that point can then be calculated. More sophisticated models take into their calculations the account of pollutant transformations and reactions in the atmosphere during the period of transport of that pollutant.

Modeling offers a number of significant benefits to the process of air quality management, some of those benefits are listed below: 1. It allows the prediction of pollutant concentrations at a very large number of ground level receptors. It is therefore possible to predict pollutant concentrations over a much wider spatial area than it have ever been possible to achieve by monitoring alone before.

2. Models can also give the benefit to predict pollutant concentrations in future years.

Many scientists have used modeling effectively to investigate pollutant concentrations at both a 'local' level (effectively within about 10-50 km of the emissions sources) and at a 'regional' level (effectively across hundreds or thousands of kilometers). Such models applications are frequently used to supplement data from monitoring networks, and to support policy decisions on likely ascendance of air quality standards and suitable control strategies (European Commission 2001).

Air pollution modeling is a numerical tool that can be used to describe the causal relationship between emissions, meteorology, atmospheric concentrations, deposition, and other factors. An air pollution measurement gives important, quantitative information about ambient concentrations and deposition, but they can only describe air quality at specific locations and times.

Air pollution models play an important role in science, because of their capability to assess the relative importance of the relevant processes. Air pollution models are the only methods that quantify the deterministic relationship between emissions and concentrations/depositions, including the consequences of past and future scenarios and the determination of the effectiveness of abatement strategies (Daly and Zannetti, 2007).

The recently developed models handle relevant data to establish an emission inventory including both stationary and mobile sources. This information system integrates in a friendly way to source information, meteorological data, monitoring measurements, and offers a tool for calculation of the emission patterns for several contaminants (Puliafito et al 2001).

5.1.1. Geographic Information Systems (GIS) Applications.

Geographical Information System (GIS) is a modern powerful tool that facilitates linking spatial data to non-spatial information (Matejicek, 2005). With its embedded relational database component, the system assists in storing, mapping and analyzing geo-referenced data in an organized structure (Manjola, et al 2010). The database and the geographical base both form the two major components of the GIS system that helps in visualizing the data in a map format.

These maps illustrate the geographical connections among the spatial variables and visually communicate geo-specific information to a decision maker. To build a spatial data model, GIS Systems support three basic types of data:

1. Vector Data, which involves,

a) Events or Points: Pattern expressed as points in space,

b) Lines: Patterns expressed as networks and

c) Polygons: Patterns expressed as analytical units with defined closed boundaries,

2. Raster data: a Grid-cell data.

3. Image: a Satellite Imagery, photographs.

The spatial analysis modeling process involves interpreting and exploring the interactions, associations and relationships among these data types specific to a geographic location. While representing a model, various elements have to be taken into consideration; those involve deriving necessary input datasets, in most of the cases, the datasets needs to be reclassified by setting a common measurement scale to the attribute variables by giving weight age depending on their influence (Yerramilli et al, 2011).

The recent development of spatial data management in the framework of geographic information systems (GISs) has created a new era of environmental modeling. More powerful computers have made running air quality models at global and local spatial scales possible.

Obviously, the use of GIS has become essential in providing boundary conditions to the air quality models. Certainly, the use of GIS in air pollution modeling can be further extended to processing the surface data. The data required for spatial models to serve air quality modeling can be grouped into few classes. (Matejicek 2005).

There are many studies all around the world that have applied GIS program to modeling their air quality researches, Bruegge and Riedel (1994), Puliafito et al (2001), Brown and Affum (2002), Kawabata and Ferreira (2003), Al-Maliky (2005), Matejicek (2005), Al-Maliky (2009), Hashim (2009), Hashim and Sultan, (2010), Al-Saadi (2012).

For the purpose to use the options offered by ArcGIS 10 program, contour lines were used (one of the spatial analyst tools) to view and analyze the concentration and distribution of the pollutants in air, soil and plant of the studied area in this research, were the models of distribution were done to demonstrate the most effected sites by those pollutants. To understand how the process of the models by ArcGIS10 takes place, to explain how the system works we need first to identify some of the process and activities that run the GIS program , those basics include .

4. IDW (ArcGIS 10)

The first element that has to be calculated is the Inverse distance weighted (IDW) interpolation which determines cell values using a linearly weighted combination of a set of sample points. This weight is a function of inverse distance. The surface being interpolated should be that of a locationally dependent variable (ESRI, 2010).

In This method it is assumed that the variable being mapped decreases in influence with the distance from its original sampled location.

- The output value for a cell using inverse distance weighting (IDW) is limited to the range of the values used to interpolate. Because IDW is a weighted distance average, the average cannot be greater than the highest or less than the lowest input. (Watson and Philip 1985).
- The best results from IDW can be obtained when sampling is sufficiently dense with regards to the local variation which is being attempting to simulate. If the sampling of input points is sparse or uneven, the results may then not sufficiently represent the desired surface (Watson and Philip 1985).
- The influence of an input point on an interpolated value is isotropic. Since the influence of an input point on an interpolated value is distance related, IDW is not "ridge preserving" (Philip and Watson 1982).
- Some input data sets may have several points with the same x, y coordinates. If the values of the points at the common location are the same, then they are considered duplicates and have no effect on

the outputs. If the values are different, then they are considered 'coincident' points (ESRI, 2010).

5. Reclassification (ArcGIS 10)

Another significant factor that is considered essential for the works and operations of GIS is the reclassification tool, which reclassifies or changes cell values to alternative values using a variety of methods. We can reclass one value at a time or groups of values at once using alternative fields; based on criteria, such as specified intervals; or by area (ESRI, 2010).

All reclassification methods are applied to each cell within a limited zone. That is, when applying an alternative value to an existing value, all the reclassification methods will apply the alternative value to each cell of the original zone. No reclassification method applies alternative values to only a portion of an input zone (ESRI, 2010). Reclassifications are done for various of different reasons some of which are listed below.

• Replacing values based on new information

Reclassification is a useful tool to replace the values in the input raster with new values. This could be due to finding out that the value of a cell should actually be a different value, for example, the land use in an area changed over time (ESRI, 2010).

• Grouping values together

Information in a raster can be simplified. For instance, a user may want to group together various types of forest into one forest class.

• Reclassifying values of a set of rasters to a common scale

Another reason to reclassify is to assign values of preference, sensitivity, priority, or some similar criteria to a raster. This may be done on a single raster or with several raster to create a common scale of values.

There are usually four steps in producing a suitability map:

- 1. Input datasets.
- 2. Derive datasets.
- 3. Reclassify datasets. Which, Reclassify each dataset to a common scale (for example, 1 to 10), giving higher values to more suitable attributes?
- 4. Weight and combine datasets, and this is can be used if necessary when Weight datasets have more influence in the suitability model which can then be combined to find the suitable locations (ESRI, 2010).

6. Cell Statistics

Calculations of cell statistics are made when it is required to calculate a statistic between multiple rasters. For instance, the use of tools to analyze a certain phenomenon over a period of time (ESRI, 2010).

5.2. Arc GIS 10 modeling for the pollutants impacts on the studied area

In this study the use of ArcGIS 10 modeling of the results of measurements of some pollutants was applied and the results of these applications are illustrated bellow.

5.2.1 Dispersion modeling of heavy metals in air

The data resulting from chemical analyses of heavy metals were used to make models of dispersion of heavy metals in air and other environmental elements (plants and soil). These results were analyzed by using the ArcGIS 10 program to get a model which can be used to represent the most affected sites of the studied area. The figures (5-1, 2, 3) represent air models of heavy metals which show that the concentrations of these pollutants increase away from the refinery at the south west part of the studied area.

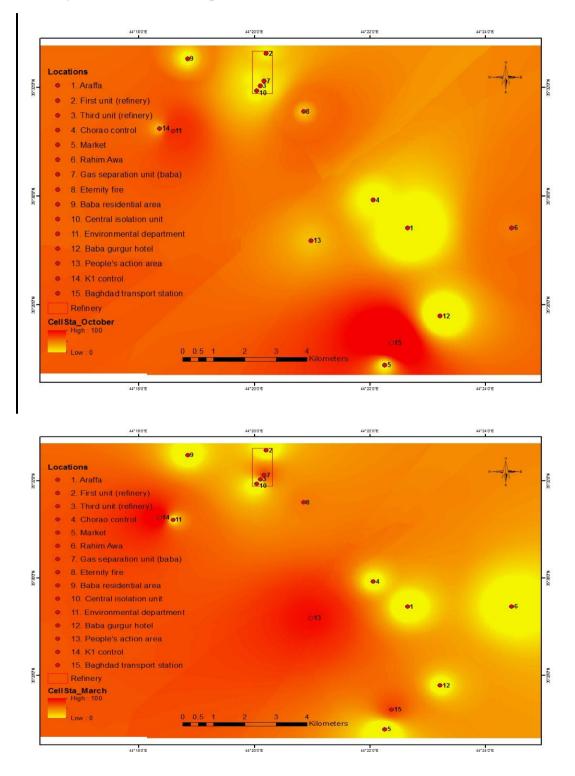


Fig. (5-1): Arc GIS model for Air pollution (heavy metals) of the studied area in October 2010(up) and March 2011(down).

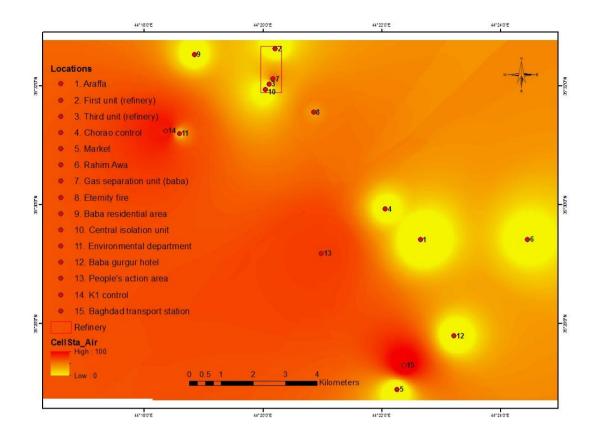


Fig. (5-2): Arc GIS model for Air modeling of heavy metals (Total)

at the studied area.

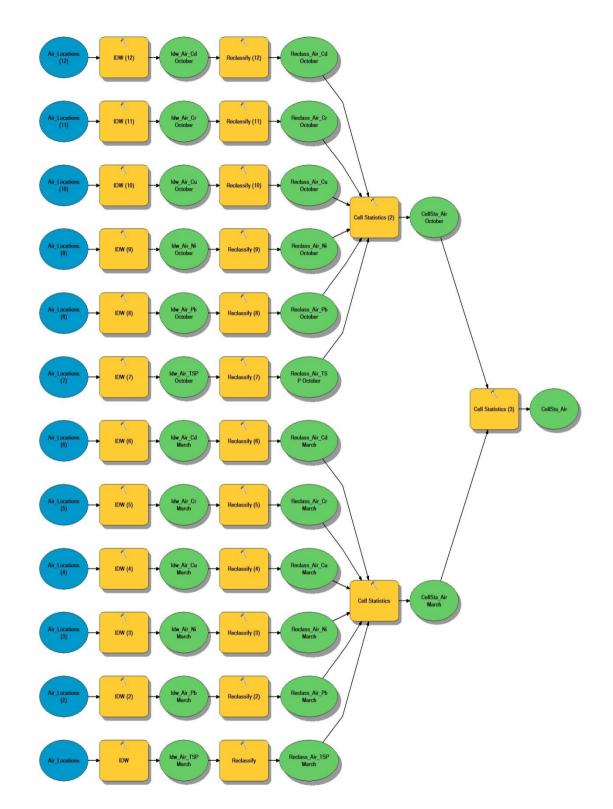
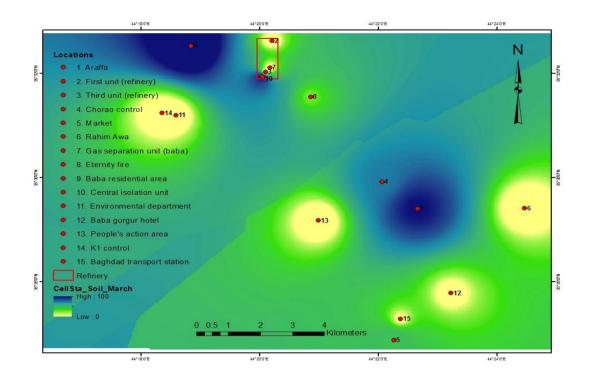


Fig. (5-3): showing the process flow charts of air pollution Arc GIS modeling.

5.2.2. Dispersion modeling of heavy metals in Soil

A similar Arc GIS modeling made to air pollutants was applied to obtain a model for heavy metals in the soil of the studied area yet this model differs from one made above because the effect of pollution distribution was much more affected by these pollutants

Figures (5-4, 5, and 6) indicate soil models of heavy metals. The concentrations of these metals increased in sites at locations near the refinery which reflects the process of oil production operation and their effect on the soil of the studied area this conclusion coincide with the study of (Salman 2007) and other site with increment reflects the other factors such as traffic intensity.



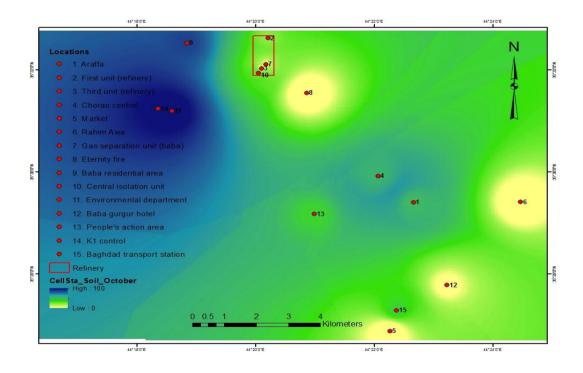


Fig. (5-4): Arc GIS model for Soil pollution (heavy metals) of the studied area in October (up) 2010 and March (down) 2011.

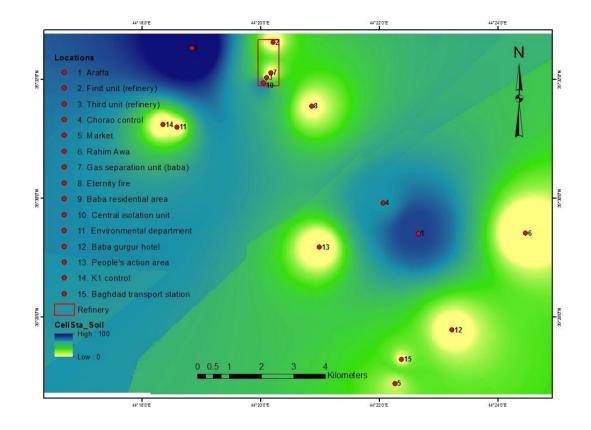


Fig. (5-5): Arc GIS model for Soil pollution of heavy metals (Total) at the studied area.

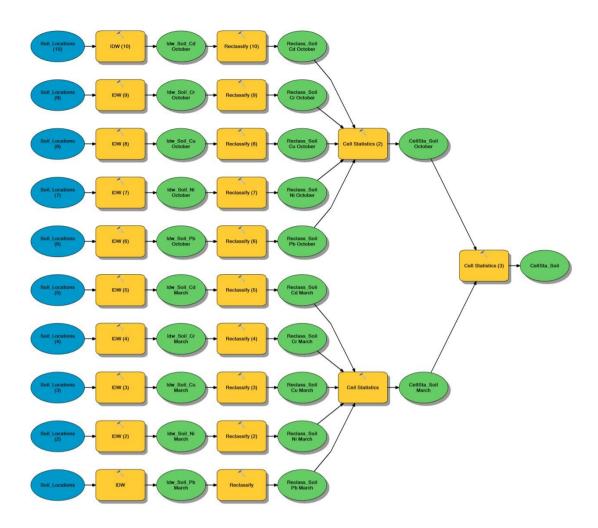
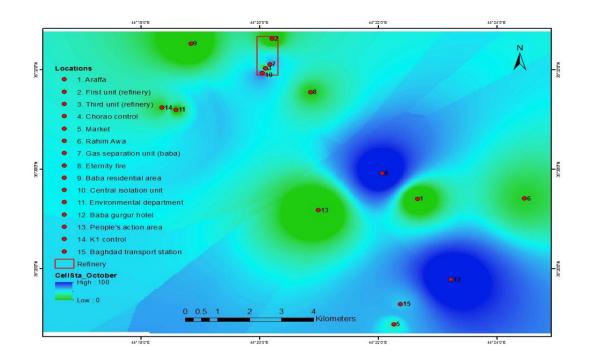


Fig. (5-6): showing the process flow charts of soil pollution Arc GIS modeling.

5.2.3. Dispersion modeling of heavy metals in Plant

The dispersion model of heavy metals in plant shows that pollutants found in plants taken from the studied area have higher concentrations of those pollutants at the sites farther from the refinery.

The factors responsible of this distribution may be the effects of meteorological elements such as wind direction and other elements or may be due to the effects of other factors other than the refinery emissions such as the emissions coming from traffic intensity and fuel combustion operation of power plants. Figures (5-7, 8, 9) represent the plant GIS model of heavy metals in plants which differs from that in air and soil models of the same sites.



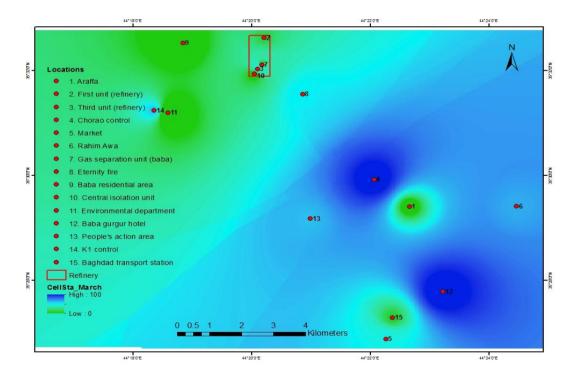


Fig. (5-7): Arc GIS model for Plant pollution (heavy metals) of the studied area in October 2010(up) and March 2011(down).

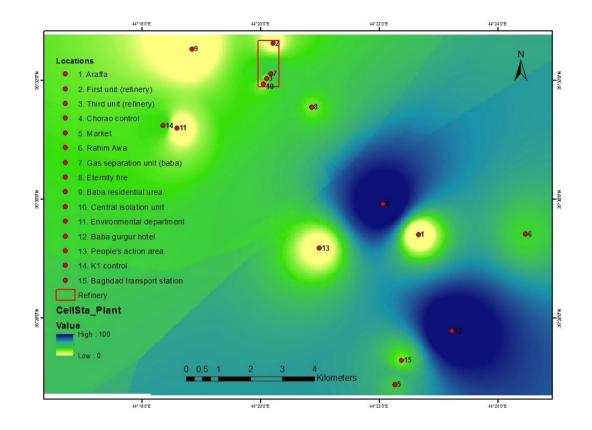


Fig. (5-8): Arc GIS model for Plant pollution with heavy metals (Total) at the studied area.

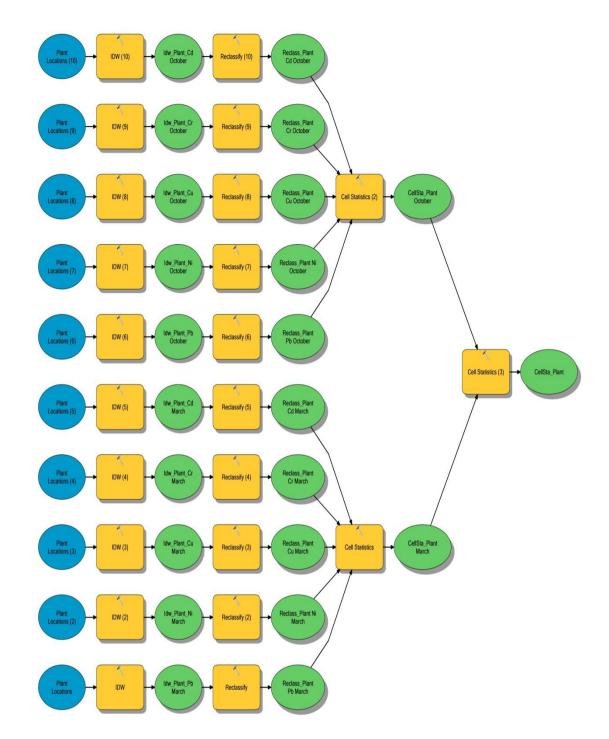


Fig. (5-9): showing the process flow charts of plants pollution in Arc GIS modeling.

5.2.4. Dispersion modeling of PAHs in air

The dispersion models of PAHs in air show that the effects of the refinery are the most effective factor on the distribution of these pollutants. The meteorological condition plays an important role to the PAHs distribution in air especially the factor of wind direction; therefore the effects of seasonal changes are obviously noticed on the model made as shown in the figures (5-10, 11, 12).

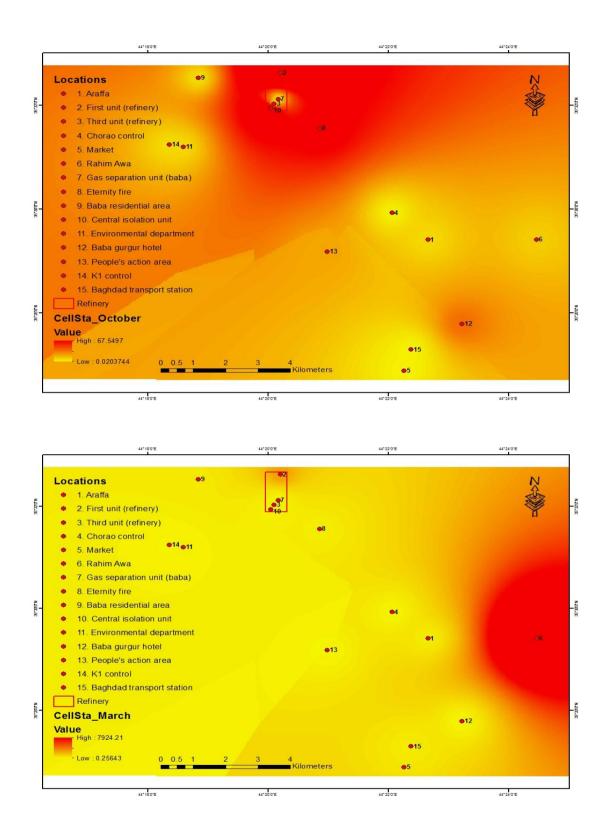


Fig. (5-10): Arc GIS model of (PAHs) pollutants in the air of the studied area in October 2010(up) and March 2011(down).

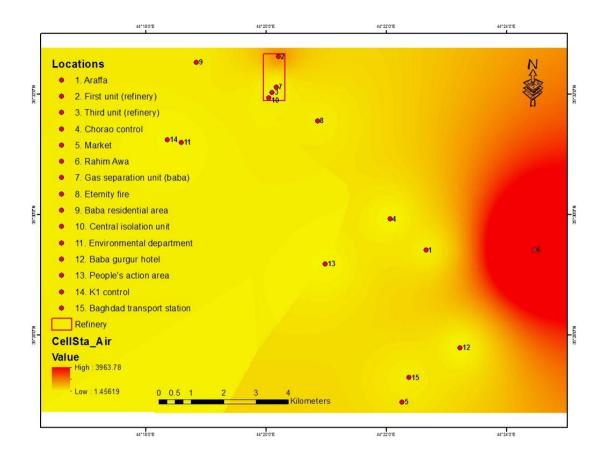


Fig. (5-11): Arc GIS model of PAHs pollutants (Total) in the air of the studied area.

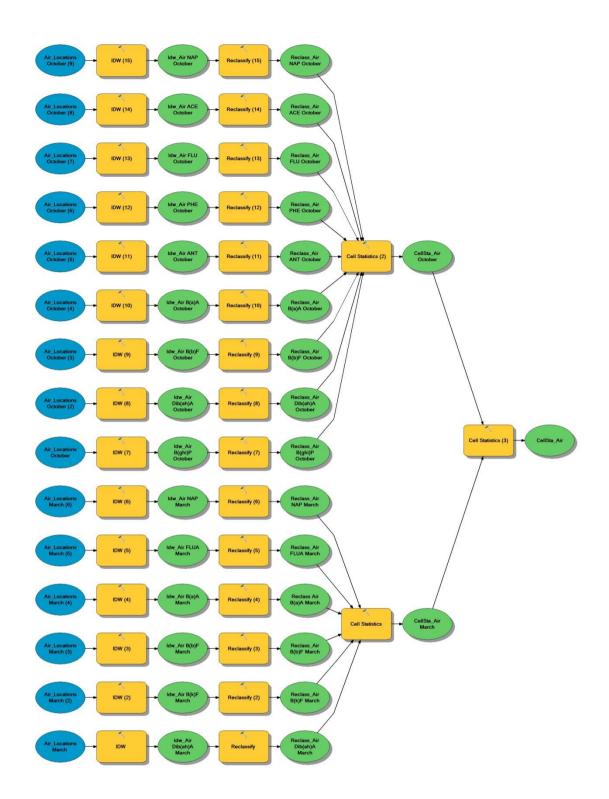


Fig. (5-12): showing the process flow charts of Air modeling for (PAHs) pollutants of the studied area.

5.2.5. Dispersion modeling of PAHs in Soil

The dispersion model of PAHs in the soil of the studied area is made using the results obtained from tested soil samples. The effect of the refinery's emissions effluents to the soil with pollutants concentrations is very clearly noticed for the sites surrounding the refinery boundaries , in addition to that , the particulate matter of big molecular weight fallen from the air as a result of their physicochemical properties and the meteorological conditions such as air temperature and rainfall is the most dominating factor in the increment of pollutant concentrations. Figures (5-12, 13and 14) shows the soil modeling of PAHs pollutants in the studied area and illustrate how these pollutants increase closer to locations around the refinery.

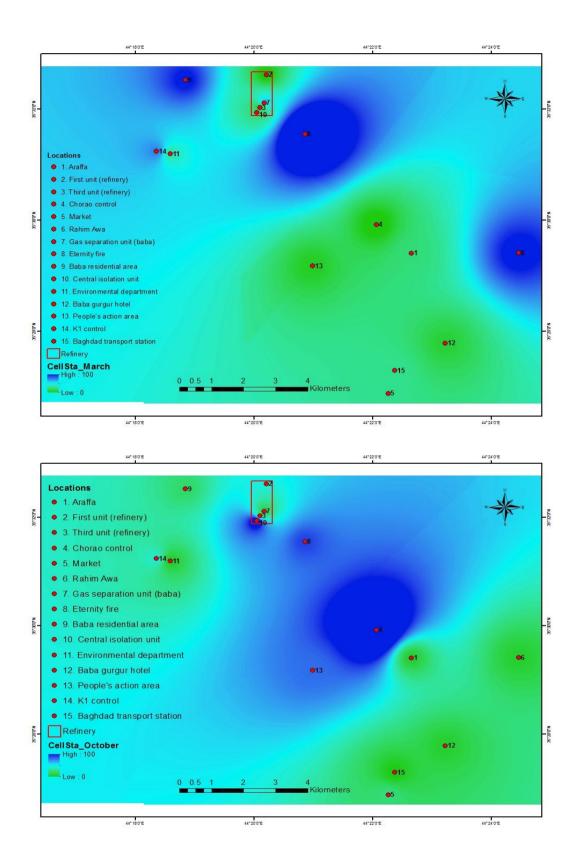


Fig. (5-13): Arc GIS model showing Soil pollution with (PAHs) for the studied area in October 2010(up) and March (down) 2011.

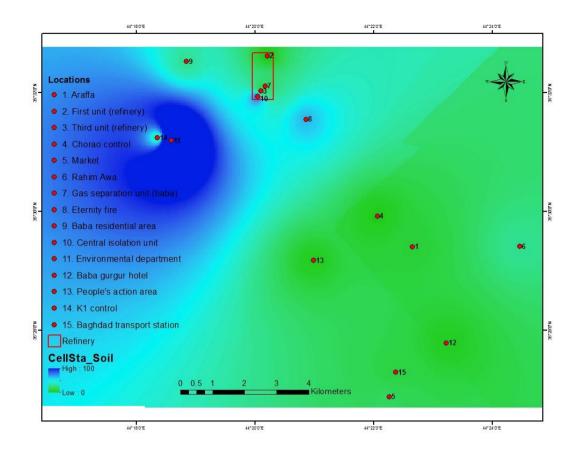


Fig. (5-14): Arc GIS model showing Soil pollution with PAHs (Total) for the studied area.

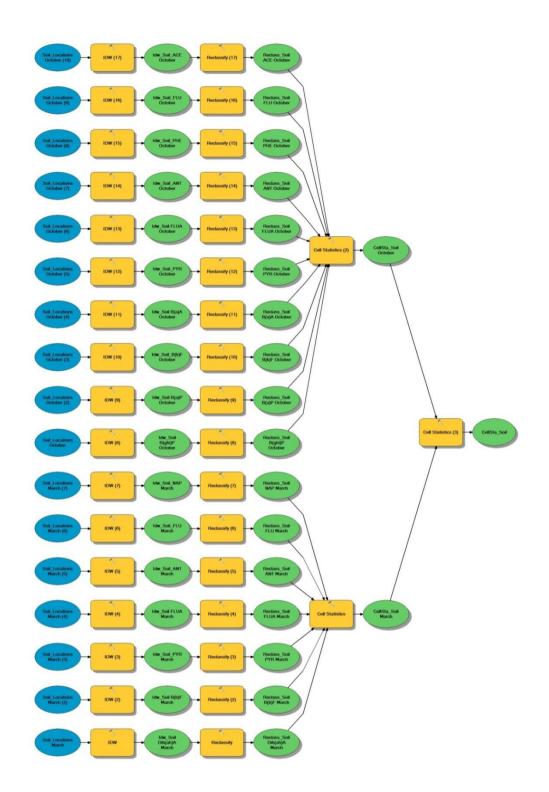
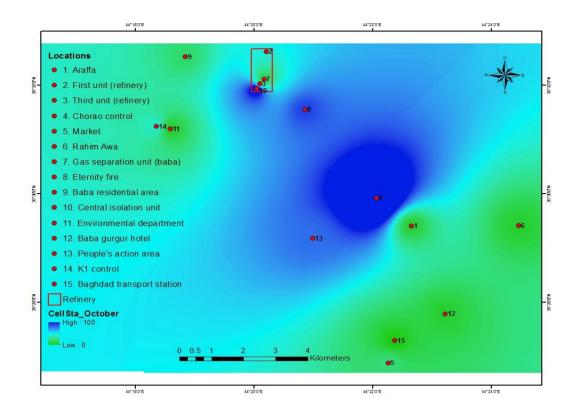


Fig. (5-15): showing the process flow charts of Soil modeling for (PAHs) pollutants of the studied area.

5.2.6. Dispersion modeling of PAHs in Plant

The dispersion model of PAHs in plant of the studied area is also made and it is found that the effects of the those pollutant concentrations can either be due to the refinery's emissions or the traffic intensity and the fuel combustion of power plants present on the sites of the studied area.

Figures (5-16, 17and 18) shows the dispersion model of the PAHs pollutants in the plants of the studied area. By using the GIS in environmental modeling. The decision can easily be made of how to control and reduce the concentration of different pollutants depending on these models.



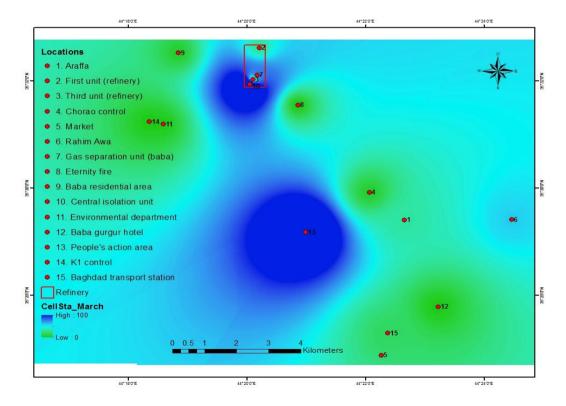


Fig. (5-16): Arc GIS model showing Plant pollutants with (PAHs) for the studied area in October 2010(up) and March 2011(down).

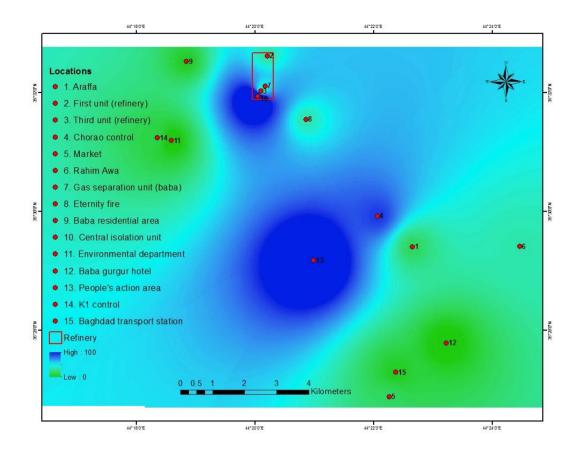


Fig. (5-17): Arc GIS model showing Plant pollutants with PAHs (Total) for the studied area.

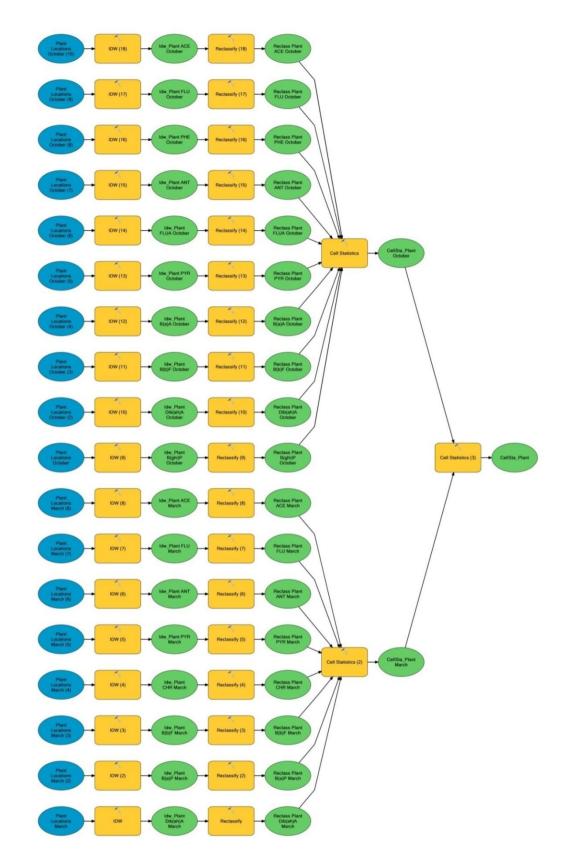


Fig. (5-18): showing the process flow charts of Plant pollution with (PAHs) in Arc GIS modeling.

Chapter Six

Conclusions and Recommendations

6.1. Conclusions

6.1.1. Air pollution

1. TSP

The concentration averages of suspended particles (TSP) in this study are higher than the permissible limits of the Iraqi National determinants of $(350 \ \mu\text{g/m}^3)$ and the world limits of $(60-90 \ \mu\text{g/m}^3)$ at the two periods: October 2010 (818.94 $\mu\text{g/m}^3$) and March 2011(829.89 $\mu\text{g/m}^3$). The little difference between the two periods reflects the little effect of the seasonal changes.

2. Gasses

1. The averages of CO compared with national and the world limits show that these averages were lower than the limits at the two periods October 2010 and March 2011. Meanwhile the concentrations of CO_2 were higher than the national and the world limits (250ppm) at the two periods for all the sites of the studied area that result may be reflect the oxidation operation of CO to CO_2 which happened at the natural meteorological conditions.

2. The average of NO_2 values was higher than the limits of national and world limits at the two periods in air of the studied area this increment reflect the increase in production operations during those periods .

3. The concentration of SO_2 in October 2010 was higher than the world limits, whereas in March 2011 no concentration of SO_2 was recorded except at one site. The decrease of SO_2 concentration at this period reflects the meteorological conditions affect especially rainfall where SO_2 become SO_3 at these periods.

3. Heavy metals

1. Comparison of the average values of lead with the national and world limits it is noticed that they are higher than these limits especially in the sites with high traffic density and fuel combustion operations that proved the partial responsibility of the refinery at this increament.

2. The concentration of Copper at the two periods were lower than the world limits. While the averages of Nickle at the two periods were higher than the world limits. The decrease of the concentration at March was due to the meteorological conditions.

4.Increasing of Chromium concentration at March period belongs to increasing of combustion fuel operation.

5. The little difference between the two averages reflects that the concentration of Cademium was not affected by seasonal changes.

4. Polycyclic aromatic hydrocarbons

The concentration of the 16 EPAs priority PAHs detected in air of the studied area in October was lower than they were in March. In addition, not all the PAHs of this study were found in all sites of measurements due to their physicochemical properties.

The increment in PAHs concentrations in March can be referred to the increase of fuel combustion operations as a result of increasing production operations of the refinery and the other factors such as the power plant.

6.1.2.Soil pollution

1.Heavy metals

1. Comparison with the world average the concentrations of Pb were lower during the two periods of measurements. The increment of Pb concentration between the two periods belongs to the increasing operations of oil production at the refinery.

2. The difference between the concentrations of copper at the two periods in averages reflects the effects of the meteorological changes especially during the rainfall were the water penetrates into the soil and removes the pollutants.

3. Nickel concentrations in soils were lower than what the world average allows. This was true for both of the periods of this study. The increment in averages of Ni and Cr between the two periods can be related to fuel combustion increment that occurred in March compared with that of October.

4. The averages of Cadmium recorded at the two periods of measurements when compared with the world allowable average it would be clear that both values were higher.

2. Polycyclic aromatic hydrocarbons

It is observed that the average of total concentrations of PAHs in March was lower than they are during October. This is a result of PAHs degradation which happen in different soils and the meteorological conditions present.

6.1.3.Plant Pollution

1.Heavy metals

1. The decrease in the concentration of Lead and Copper in Eucalyptus leaves from October to March is related to its concentration in air at the same period which may be referred to the meteorological elements which occur during different seasons.

2. The increment of Nickel concentration that was found between the two averages, link should be made with the fuel combustion operations of the refinery, this conclusion is supported if compared with the concentrations found earlier in the soil at the same period.

4. Meteorological condition have a great role in making the difference of averages of Cr obtained between the two periods. The other dominating factor affecting the results is the distribution of heavy metals which differs at the sites of the studied areas.

5. It becomes clearly obvious that during the two periods the meteorological changes on the concentration of (Cd) in plant of the studied area is apparent.

2. Polycyclic aromatic hydrocarbons

The average of total concentrations of PAHs in March was higher than they are during October; this is due to air temperatures decrease during the fall and winter season which may be deposited PAHs on the plant leaves and possibility to absorb by plants .

6.2. Recommendations

1. Developing a treatment system to the different units of the refinery to reduce environmental pollution as a result of the divorced emitted by these units so as to minimize or reduce the impact of these pollutants.

2. Making a tests and environmental measurements periodically to determine the concentration of pollutants resulting from the refinery and other sources.

3. Introducing a new legislation aimed to reduce the rates of environmental pollutants and work on the application of such legislation.

4.Increasing vegetation and planting areas with bare soil surrounding the refinery and North Oil Company to reduce the rates of pollutants emitted from them into the environment.

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

6.Accelerating the development of the local power system to reduce the continued reliance on the use of generators as an alternative to electric power and thus reduce pollution.

7. Expand the use of geographic information system (GIS) and employment possibilities in this system in Environmental Studies.

References

- Abdel Wahid A.A., (2005):Effect of Atmospheric Factors on Some of Air Pollutants in Al-Andalus and Al-Wazeeriya Stations in Baghdad. MSc. thesis ,College of science, AL-Mustansirya university.
- Afaj, Adnan Hassan et al, (2000): a study of air pollution in the refinery of Baiji, Department Environmental Research, the Atomic Energy Organization. (In Arabic).
- Afaj, A. H.et al (2008): Environmental Impact of Air Pollution in AL-Daura Refinery.
- Ahrens, C.D., 2005." Essentials of Meteorology :An Invitation to the Atmosphere".3th Edition, Cambridge University Press, p.463.
- Ali H. A., (2007) : Heavy Metals Concentrations in Surface Soils of the Haweja Area South Western of Kirkuk, IRAQ. Journal of Kirkuk University– Scientific Studies , vol. 2 , no. 3.
- Al-Hamdany O.J., (2000): A study on gasses emission from the burner and their effects on environmental pollution. College of Education, AL-Basra University.
- AI- Maliki, M. A. S., (2005): Evaluation of air pollutants, water and soil in the city of Baghdad, using geographic information system (GIS), PhD thesis, Faculty of Science, Baghdad University, (171) page. (in Arabic)
- AI- Maliky R.N., (2006): Effect of Air Pollution on Some Plants in Baghdad City. MSc. Thesis, College of Science, AL-Mustansirya university.99p.(in Arabic).
- AI- Maliky R.N., (2009): Biogeochemical Assessment of some heavy metals in AI-Hammar marsh by using GIS. PhD. Thesis . College of Science for Women, University of Baghdad. 170 p.
- AI-QaisyA.T.and AI-Shammary M.A.(1997): study of the petroleum pollutants of north oil company fields central and northern Iraq, northern oil company, geology department (in Arabic).
- AI- Rawi N.L., (1997): The environmental pollution features and treatment in north oil company. Oil and Environment Symposium, North Oil Company, Ministry of Oil.
- AI-Saadi G.M. (2012): Assessment of Air and Water Pollution Due To Operation South Of Baghdad Power Plant. MSc. Thesis, Building and Construction Engineering Department University of Technology.147p.
- AL-Saadi, Ahmed Nama (1999): air pollutionin the city ofBaghdadand its suburbs withcarbon monoxideand heavy metals.Master Thesis (unpublished), College of Science, University ofBaghdad, 118p.

- AI-SamaraeeO.S., (2006): Assessment of Lead Pollution at gasoline service stations in Baghdad city. Unpublished MSc. Thesis, AL-Mustansirya University, College of engineering, Baghdad, Iraq.
- Al-Tikriti, S. A.,(1997): Effect of air polluted industrial projects on the environment of the city. A case applied study on power plant of AL-Dura and south of Baghdad. Unpublished PhD. Thesis, University of Baghdad.
- Alves C.A., Vicente A., Evtyugina M., Pio C.A., Hoffer A., Kiss G., Deccsari S., Hillamo R. and Swietlicki E. ,(2009): Characterisation of Hydrocarbons in Atmospheric Aerosols from Different European Sites. World Academy of Science, Engineering and Technology 57.
- Asgari K. and Amini H., (2011): Biomonitoring of Trace Element in Air and Soil Pollution by Using Acacia. Journal of Research in Agricultural Science, Vol. 7, No. 2, pages: 115-124.
- Assadi A., Pirbalouti A. G., Malekpoor F., Teimori N. and Assadi L., (2011) : Impact of air pollution on physiological and morphological characteristics of *Eucalyptus camaldulensis*Den. Journal of Food, Agriculture & Environment Vol.9 (2) : 676 - 679.
- Bari M., Baumbach G., Kuch B. and Scheffknecht G., (2011) : Particlephase concentrations of polycyclic aromatic hydrocarbons in ambient air of rural residential areas in southern Germany, springer quotes.
- Bradley L. J. N., Magee B. H. and Allen S. L., (1994): Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils. Journal of Soil Contamination, 3(4)
- **Brown A.L. and Affum J.K. (2002)**: A GIS-based environmental modelling system for transportation planners. Computers, Environment and Urban Systems. 26 : 577–590.
- BrueggeB.and Riedel E., (1994): A Geographic Environmental Modeling System:Towards an Object-Oriented Framework.Proceedings of the European Conference on Object-Oriented Programming (ECOOP-94), Lecture Notes in Computer Science, Springer Verlag, Volume #821, pp 474-492.
- Bryselbout, C., Henner, P., Carsignol, J. andLichtfouse, É. (2000):Polycyclic aromatic hydrocarbons in highway plants and soils. Evidence for a local distillation effect, ANALUSIS, 2000, 28, N° 4.
- Buday, T. and Jassim, S. Z., (1987): The regional geology of Iraq, Vol. 2, Tectonism, Magmatism and metamorphism, p352.
- Burt, R.; Wilson, M.A.; Mays, M.D. and Lee, C.W., (2003): Major and trace elements of selected pedons in the USA, published in Jonrnal of Environ. QualityIn Salman (2007).
- Buszewski B., Jastrzębska A., Kowalkowski T. and Górna-Binkul A(2000):Monitoring of Selected Heavy Metals Uptake by Plants and Soils in the Area of Toruń, Poland. Polish Journal of Environmental Studies Vol. 9, No. 6, 511-515.
- CAOBISCO (1996), Heavy metals.

- Commentary (2003), Heavy metals and plants –model systems and hyperaccumulators.New Phytologist**159**: 289–293.
- Daly A. and Zannetti P., (2007): Air Pollution Modeling An Overview. Chapter 2 of AMBIENT AIR POLLUTION.
- **Dawood S.K., (2003)**: Specific Study for the Pollution Percentage with Polycyclic Aromatic Hydrocarbons in the Iraqi Heavy Oil Shale and for Wheat infected with the Telletia. MSc. Thesis, College of Science, University of Baghdad.
- Deabreu, C. A.; Raid, B. V.; Deabreu, M. F. and Gonzalez, A. P., (2005): Routine soil testing to monitor heavy metals and Boron, Sci. Agric. (piracicaba, Braz.), Vol. 62, No. 6, pp. 564-571 In Salman (2007).
- Ding X., Wang X., Xie Z., XiangC., Mai B., Sun L., Zheng M., Sheng G., Fu J. and PÖschlU.(2007): Atmospheric polycyclic aromatic hydrocarbons observed over the North Pacific Ocean and the Arctic area: Spatial distribution and source identification. Atmospheric Environment 41 :2061–2072.
- **Dixon E.A., (2005)**: Measurement of Exposure to Emissions From Sour, Solution Gas Flares, Using Biomonitoring Methods. Environmental Science Program and Department of Chemistry/ University of Calgary.
- Dzepina K., Arey J., Marr L.C., Worsnop D.R., Salcedo D., Zhang Q., Onasch T.B., Molina L.T., Molina M.J. and Jimenz J.L., (2007): Detection of particle-phase polycyclic aromatic hydrocarbons in Mexico City using an aerosol mass spectrometer, International Journal of Mass spectrometry ,263 : 152-170.
- ESRI, (2010): The Manual of Arc GIS 10.
- **European Commission, (2001)**: Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH). Position Paper.
- Fugas M. and De Koningh W., (1991): Comparative Analysis of Indoor and Outdoor TSP Concentrations in Bombay, Toronto, and Zagreb. Methods for Assessing Exposure of Human and Non-Human Biota. Edited by R.G. Tardiff and B. Goldstein. John Wiley & Sons Ltd.
- Habib H. R.,.Awadh S.M. and Muslim M. Z., (2012): Toxic Heavy Metals in Soil and Some Plants in Baghdad, Iraq.Journal of Al-NahrainUniversity. Vol.15, No.2, pp.1-16.
- Halek F., et al,(2006): Particulate Polycyclic Aromatic Hydrocarbons in Urban Air of Tehran, J. Environ. Health. Sci. Eng., Iran., Vol. 3, No. 3, pp. 247-254.
- Harrison, R. M. (1992): Pollution: Causes, Effects and Control, Second Edition. Cambridge: The Royal Society of Chemistry.in AL-Saadi 2012.

- Hashim B.M., (2009): Measurement and study concentrations some air pollutants in Baghdad city. MSc thesis College of Science AI Mustansiriyah University in Atmospheric Sciences. 95p.
- Hashim B. M. and Sultan M. A., (2010): Using remote sensing data and GIS to evaluate air pollution and their relationship with land cover and land use in Baghdad City.Iranian Journal of Earth Sciences 2 / 20-24.
- Hays M. D., Smith N. D., Kinsey J., Dongb Y. and Kariherb P., (2003): Polycyclic aromatic hydrocarbon size distributions in aerosols from appliances of residential wood combustion as determined by direct thermal desorption—GC/MS. J. Aerosol Science 34 :1061–1084.
- Henner P., Schiavon M., Morel J. and Lichtfouse E., (1997) : Polycyclic aromatic hydrocarbons (PAH) occurrence and remediation methods. Analusis Magazine 25, M56-M59.
- Hou X., Zhuanga G., Suna Y. and Anc Z., (2006): Characteristics and sources of polycyclic aromatic hydrocarbons and fatty acids in PM2.5 aerosols in dust season in China. Atmospheric Environment 40, 3251–3262.
- Huang X., El-Alawi Y., Penrose D. M., Glick B. R. and GreenbergB. M. (2004): A multi-process phytoremediation system for removal of polycyclic aromatic hydrocarbons from contaminated soils. Environmental Pollution 130: 465-476.
- Husain K.I. (2003):Separation and Determination of Polycyclic Aromatic Hydrocarbons in Iraq Environmental Samples.PhD. Thesis, College of Education– Ibn Al-Haitham, University of Baghdad.104 p.
- Iraqi Meteorological Organization, 2011: Values of maximum and Minor temperatures, rainfall, relative humidity, wind speed and direction in Kirkuk station for period from (2002- 2011).Unpublished data, Department of Climate.
- Iraqi Ministries of Environment and Water Resources (2006): New Eden Master Plan for Integrated Water Resources Management in the Marshland Area. Volume 1- Book 1. Italy – Iraq.
- Jan,J.et al,(2000): Evaluation of Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Plants, The potential use of PAH accumulation as a marker of exposure to air emissions from oil and gas flares. ISBN 0-7785-1228-2. Report prepared for the Air Research Users Group, Albert Environment, Edmonton, Alberta.
- JawadA.M., (1998): The Iraqi oil derivatives and their impacts on the environmental pollution. Department Studies and Planning Continue, Ministry of Oil, Iraq.
- Jing Y., Gao B., Jing Y. and Ma Z., (2011): Potential ecological risk assessment of soil heavy metals contamination around coal gangue piles of Baodian coal mine area of Shandong, China.
- Jolly W. and SA T., (2007): Anthropogenic Aerosols and Climate Change, An Alternative view,

- Kanbour, F. and Yassin, SH., (1985): Suspended Particulates in the Air of Al-Noor Factory for dry Battery. Proceedings of Symposium on Environmental ProtectionFrom Industrial pollution, 13-16 May. Baghdad. Iraq
- Kawabata M. and Ferreira Jr. J., (2003): GIS Modeling of Urban Components to Monitor and Model Urban Respiration .CSIS Discussion Paper No. 58.
- Kos B., Grčman H. and Leštan D., (2003): Phytoextraction of lead, zinc and cadmium from soil by selected plants. Plant Soil Environ., 49, (12): 548–553.
- Kozanecka T., Chojnicki J. and Kwasowski W., (2002): Content of Heavy Metals in Plant from Pollution-Free Regions. Polish Journal of Environmental Studies Vol. 11, No. 4, 395-399.
- Lawal A.O., BatagarawaS M., OyeyinkaO. D. and Lawal M. O., (2011):Estimation of Heavy Metals in Neem Tree Leaves along Katsina – Dutsinma – Funtua Highway in Katsina State of Nigeria. J. Appl. Sci. Environ. Manage. Vol. 15 (2) 327 – 330.
- Leili M.,NaddafiK.,Nabizadeh R.&YunesianM. (2008):The study of TSP and PM₁₀ concentration and their heavy metals content in central area of Tehran, Iran.Airuality atoms health, 1: 159-166.
- Li Y., Liu Z., Zhao X., Li H. and Li H., (2010): Evaluation on Potential Ecological Risk of Heavy Metal Pollution in Sediment of Urban Sewage River, National Basic Research Program and National Natural Science Foundation of China.
- Lim M. C. H., Ayoko G. A. and Morawska L., (2005): Characterization of elemental and polycyclic aromatic hydrocarbon compositions of the urban air in Brisbane. Atmospheric Environment 39 (3):pp. 463-476.
- Lindsay, W. L., 1979: Chemical equiliberia of soils, John Wiley and sons, p449(In Salman 2007).
- Liu L., Hashi Y., Liu M., WeiY. and Lin J., (2007):Determination of Particleassociated Polycyclic Aromatic Hydrocarbons in Urban Air of Beijing by GC/MS, Analytical Sciences, Vol. 23. The Japan Society for Analytical Chemistry.
- **MAJEED N. N.**, (2004): Geotechnical study of gypseous soil chosen from places in Kirkuk city . PhD. Thesis, College of Sciences, University of Baghdad .
- ManjolaB., ElvinC., BledarM.andAlbanaZ., (2010): Mapping Air Pollution in Urban Tirana Area Using GIS. International Conference SDI In :Yerramilli A., Dodla V. B. R. and Yerramilli S.,(2011).
- Masitah A., Zaini H., and Lee S. K.,(2007): PM10 and Total Suspended Particulates (TSP) Measurements in Various Power Stations, The Malaysian Journal of Analytical Sciences, Vol 11, No 1: 255-261.

- Matejicek L., (2005): Spatial modelling of air pollution in urban areas with GIS: a case study on integrated database development. Advances in Geosciences, 4, 63–68.
- MaxwellJ. A., (1968): Rock and Mineral analysis, Jhon Wiley and sons, N. Y., p584(In Salman, 2007).
- Mesdaghinia A.,(2008): The study of TSP and PM10 concentration and their heavy metal content in central area of Tehran, Iran, Air QualAtmos Health (2008) 1:159–166.
- **Ministry of Environment,**(**2008**): Determinants of local and global air pollutants. Report and the reality of the situation, the air quality department.
- Mohammed F. A., (2009): Pollution Caused by Vehicle Exhausts and Oil Trash Burning in Kirkuk city. Iraqi Journal of Earth Sciences, Vol.9, No. 2, pp 39-48.
- Mosa A.H., (2000): Environmental pollution, Contemporary Thought House - Beirut, The first editionin. In Hashim, (2009).
- Mudgal V., Madaan N. and Mudgal A., (2010): Heavy metals in plants: phytoremediation: Plants used to remediate heavy metal pollution. Agriculture and Biology Journal of North America, ISSN Print: 2151-7517.
- Naveed N.H., Batool A. I., Ur Rehman F. and Hameed U., (2010): Leaves of roadside plants as bioindicator of traffic related lead pollution during different seasons in Sargodha, Pakistan. African Journal of Environmental Science and Technology Vol. 4(11), pp. 770-774.
- **Newsletter Year (2003**): Polycyclic Aromatic Hydrocarbons (PAHs) In Air And Their Effects On Human Health -November 2003.
- Oancea S., Foca N. and Airinei A., (2005): Effects of Heavy Metals on Plant Growth and Photosynthetic Activity, Tomul I, s. Biofizică, FizicămedicalăşiFizicamediului.
- Oleszczuk P. and Baran S., (2007) : Polyaromatic Hydrocarbons in Rhizosphere Soil of Different Plants: Effect of Soil Properties, Plant Species, and Intensity of Anthropogenic Pressure. Communications in Soil Science and Plant Analysis, 38: 171–188.
- Onder S., Dursun S., Gezgin S. and Demirbas A., (2007): Determination of Heavy Metal Pollution in Grass and Soil of City Centre Green Areas (Konya, Turkey).Polish J. of Environ. Stud. Vol. 16, No. 1,145-154.
- Othman M.Y., Jassim W.M., Abbas M.S. and Hasan H.N. (1998a): The effect of the industrial gasses whom effluents from the north gas complex on the environmental pollution at the around area, The Northern Gas Company (in Arabic).

- Othman M.Y., Aziz N.A., Hasan H.N., Tawfiq N.B. and Murad I. H., (1998b): the effect of industrial polluted gasses released from north gas complex on the workers' health, The Northern Gas Company (in Arabic).
- Page A.L., Miller R.H., and Kenney D.R.,(1982): Methods of Soil Analysis. Part 2 Chemical and Biological Properties. Amer. Soc. Agron. Inc. publisher, Madison. Wisconsin.
- Palmberg C., (2002), Annotated Bibliography on Environmental, Social and Economic Impacts of Eucalypts .Working Paper FP/17E, FAO, Rome (Italy).
- Paul M. White, JR., Wolf D. C., Thoma G. J., and Reynolds C. M., (2006): Phytoremediation of Alkylated Polycyclic Aromatic Hydrocarbons in A crude Oil Contaminated Soil . Water, Air, and Soil Pollution ,169: 207–220.
- **Pearson M., (1995)**: Effects of ozone on growth and gas exchange of *Eucalyptus globules* seedlings. Tree Physiology 15, 207–210.
- Peter, S., 2004: Geochemical factors controlling the migration and immobilization of heavy metals as reflected by the study soil profiles from the Cserhatmts., Lab. For Geochemical research, Hungarian Academy of sciences, Budapest, p17(In Salman 2007).
- Philip, G. M., and Watson D. F. (1982): A Precise Method for Determining Contoured Surfaces. Australian Petroleum Exploration Association Journal 22: 205–212.
- Puliafito E., Guevara M. and Puliafito C., (2001):Modelling air pollution in an industrial area using GIS as an assessment tool, International Conference in Air Pollution, Ancona, Italia.
- Ravindra K., Sokhi R. and Grieken R. V., (2008), Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation, Atmospheric Environment.
- Sabry A.A. (2007): An Analytical Study of Separation and Determination of Poly aromatic Hydrocarbons in Raw and Drinking Water Using the Reversed-Phase HPLC Technique. MSc. Thesis, College of Education– Ibn Al-Haitham, University of Baghdad.74 p.
- Salman, K.H. (2007):Study in the Environmental Situation for Al-Basra Governorate. PhD thesis, College of Science, Baghdad University, (180) page. (in Arabic).
- **Sufuan, SA.A.,(1990)**: Modeling of Air Pollution DispersionFrom Elevation Sources . M. Sc. Thesis. College of Engineering . University of Baghdad.
- Seyyednejad S. M. and Koochak H. (2011) : A Study on Air Pollution effects on *Eucalyptus camaldulensis*. International Conference on Environmental, Biomedical and Biotechnology.IPCBEE vol.16, Singapoore
- Shihua QI., et al, (2001): Distribution of Polycyclic Aromatic Hydrocarbons in Aerosols and Dust fall in Macao .Environ.Monitoring and Assessment. Vol.72,pp.115-127.
- Sissakian V.K., (1993): The Geology of Kirkuk Quadrangle, states

Establishment of Geological survey and mining Geosurv, Report

c-2229.

no.

- Suciu I., Cosma C., Todică M., Bolboacă S. D. and Jäntschi L., (2008): Analysis of Soil Heavy Metal Pollution and Pattern in Central Transylvania. Int. J. Mol. Sci. 9, 434-453.
- **Tang**, **X.L.,Bi,X.H.,Sheng,G.Y., Tan,J.H.** and **Fu**, **J.M.,(2006)**:Seasonal variation of the particle size distribution of *n*-Alkanes and polycyclic aromatic hydrocarbons (PAH's) in urban aerosol of Guangzhou, China ,Environmental monitoring and assessment,117:193-213.
- **Taylor E. T. and Nakai S., (2012)**:Monitoring the levels of toxic air pollutants in the ambient air of Freetown, Sierra Leone, African Journal of Environmental Science and Technology Vol. 6(7), pp. 283-292.
- USDA. ,(2000), Heavy Metal Soil Contamination, Soil Quality Urban Technical Note No. 3.
- VenkataramanC. ,Negi, G., Sardar , S.B. and Rastogi, R..(2002): Size distributions of polycyclic aromatic hydrocarbons in aerosol emissions from biofuel combustion ,J.of Aerosol Science ,33 : 503-518.
- Wanjura J. D., Shaw, B. W., Parnell C. B., Jr., Lacey R. E. and Capareda S. C., (2008): Comparison of Continuous Monitor (TEOM) and Gravimetric Sampler Particulate Matter Concentrations. American Society of Agricultural and Biological Engineers, Vol. 51(1): 251-257.
- Watson, D. F., and Philip G. M.(1985): A Refinement of Inverse Distance Weighted Interpolation. Geoprocessing 2:315–327.
- WHO (1996): revised WHO Air Quality Guidelines For Europe.
- **WHO (2000)**: Air Quality Guidelines Second Edition. WHO Regional Office for Europe, Copenhagen, Denmark.
- Xie M., Xie F., Deng Z. and Zhuang G.,(2003): Determination of polynuclear aromatic hydrocarbons in aerosol by solid-phase extraction and gas chromatography_ mass spectrum. Talanta60 :p 1245_ 1257.
- Yap D.W., Adezrian J., Khairiah J., Ismail B.S.and Ahmad-Mahir R., (2009):The Uptake of Heavy Metals by Paddy Plants (*Oryza sativa*) in Kota Marudu, Sabah, Malaysia. American-Eurasian J. Agric. & Environ. Sci., 6 (1): 16-19.
- Yassen M. E. and JAHI J. MD., (2007): Investigation of Variations and Trends in TSP Concentrations in The Klang Valley Region, Malaysia. Malaysian Journal of Environmental Management 8: 57 – 68.
- Yerramilli A., Dodla V. B. R. and Yerramilli S.,(2011): Air Pollution, Modeling and GIS basedDecision Support Systems for Air Quality Risk Assessment.Earth and Planetary Sciences, Oceanography and Atmospheric

Sciences "Advanced Air Pollution", book edited by FarhadNejadkoorki, ISBN 978-953-307-511-2, Published

Zitka O., Babula P., Sochor J., Kummerova M., Krystofova O., Adam V., Havel L., Beklova M., Hubalek J. and Kizek R.,(2012):Determination of Eight Polycyclic Aromatic Hydrocarbons and in Pea Plants (*PisumsativumL.*) Extracts by High Performance Liquid Chromatography with Electrochemical Detection. Int. J. Electrochem. Sci., 7,908 – 927.

المستخلص

تتأثر العناصر البيئية المختلفه (الهواء . التربه والنبات) في العديد من المواقع ضمن مصفى كركوك بالتلوث بالهيدروكربونات العطرية المتعددة الحلقات والعناصر الثقيلة. وهذا التلوث يؤثر بطريقه مباشرة وغير مباشرة على الصحة العامه . جمعت العينات البيئية من ١٦ موقعا مختارا داخل وخارج المصفى لتقييم التلوث البيئي الناجم من مطلقات المصفى الى البيئه في المناطق المحيطه ووضع خرائط لتوزيع الملوثات في المواقع المدروسه وعمل موديلات لطريق توزيع وانتشار الملوثات وكانت النتائج كما يلي

كانت معدلات تركيز الدقائق العالقة (TSP) المسجلة في هذه الدراسة أعلى بكثير من الحدود المسموح بها للمحددات الوطنية و العالمية لكل من : تشرين الاول ٢٠١٠ وآذار ٢٠١١.

كانت معدلات تراكيز غاز أول اوكسيد الكاربون CO اقل من المحددات الوطنيه والعالميه وسجلت اعلى التراكيز في المواقع البعيده عن المصفى ، اما تراكيز غاز ثاني اوكسيد الكاربون كانت اعلى من المحددات الوطنيه والعالميه في جميع المواقع ولكلا الموسمين. كانت تراكيز غاز ثنائي اوكسيد الكاربون كانت اعلى من المحددات الوطنيه والعالميه في جميع المواقع ولكلا الموسمين. كانت تراكيز غاز ثنائي اوكسيد النتروجين اعلى بقليل من المحددات الوطنيه والعالميه في معددات الوطنيه والعالميه في معدم مع المواقع ولكلا الموسمين. كانت الكاربون كانت اعلى من المحددات الوطنيه والعالميه في جميع المواقع ولكلا الموسمين. كانت تراكيز غاز ثنائي اوكسيد النتروجين اعلى بقليل من المحددات الوطنيه والعالميه. معدل تركيز غاز ثنائي اوكسيد النتروجين اعلى بقليل من المحددات الوطنيه والعالميه واقل من المحددات الوطنيه الموسيد الكبريت في مواقع الدراسه عدا موقعا واحدا حيث كان تركيزه (0.1ppm .

وجد ان تركيز الرصاص في الهواء لمنطقة الدراسة في تشرين الاول اعلى من الحدود المسموحه في حين كان تركيز الرصاص في آذار أقل من الحدود الوطنية والعالمية هذا الانخفاض في تركيز الرصاص يعكس تآثير الظروف الجوية خلال هذه الفترة. اما النحاس فكان تركيزه في الهواء خلال الفترتين أقل من الحدود المسموح بها ، بينما كان تركيز النيكل أعلى من المحددات القياسية ، كما وجد أن معدل الكروم في الهواء ضمن منطقة الدراسة كان متقاربا لكل من فترتي القياس وهذا يثبت أن التغيرات الموسميه ليس لها تاثير على تركيز هذا العنصر.

كان اعلى تركيز للهيدروكاربونات العطريه متعددة الحلقات في هواء منطقة الدراسة في تشرين الاول (µg/m3٦٧,٦٨٥) في حين كان اعلى تركيز في آذار كان (µg/m3٦٧,٦٧٥) (µg/m3). ويمكن ان تعزى الزيادة في تركيز الهيدروكربونات العطرية متعددة الحلقات في هذه الفترة إلى زيادةة عمليات احتراق الوقود الناتجه من زيادة عمليات الانتاج اضافه الى استخدام مولدات الطاقة التي تعمل على نحو متزايد خلال أشهر الشتاء.

وجد ان تركيز الرصاص في التربة ضمن منطقة الدراسة كان أقل خلال فترتي القياسات مقارنة مع المعدلات العالميه . تركيز النحاس كان أقل من المعدلات المسموح بها عالميا . اما تركيز النيكل في التربة فقد كان أقل من االمعدل العالمي المسموح و لكلا الدراسة. وقد ازداد تركيز الكروم في التربة خلال شهرآذار. في حين كان تركيز الكادميوم أعلى من الحدود العالميه المسموحة.

كان معدل تركيز الهيدروكاربونات العطريه متعددة الحلقات الكلي في تربة منطقة الدراسة في آذار (ppb۲٦,٩٢) وذلك من معدلها في تشرين الاول (ppb۲٦,٩٢) وذلك نتيجة للظروف الجوية مثل تساقط الامطار، درجة الحرارة، والرياح السائدة .

معدل تركيز الرصاص والنحاس في أوراق الكالبتوس التي اخذت من منطقة الدراسة سجل انخفاضا بين تشرين الاول و آذار بسبب تأثير العناصر الجوية في المواسم المختلفة. ازداد تركيز النيكل في اوراق الكالبتوس المأخوذة من منطقة الدراسة بين الفترتين بسبب زيادة عمليات احتراق الوقود الناتجه من مطلقات المصفى وحقول النفط بالقرب من منطقة الدراسة. تم قياس تركيز (الكروم) في أوراق الكالبتوس في النباتات الموجودة في منطقة الدراسة ولوحظ انخفاض التركيز (الكروم) في أوراق الكالبتوس في النباتيات الموجودة في منطقة الدراسة ولوحظ انخفاض التركيز (الكروم) في أوراق الكالبتوس في النباتات الموجودة في منطقة الدراسة ولوحظ انخفاض التركيز بين الفترتين بسبب الظروف الجوية خاصة سقوط المطر و سرعة واتجاه الرياح التي أوراق الكالبتوس في النباتات الموجودة في منطقة الدراسة ولوحظ انخفاض التركيز بين الفترتين بسبب الظروف الجوية خاصة سقوط المطر و سرعة واتجاه الرياح التي أوراق الكالبتوس أوراق المعدلات التي تم الحصول عليها. وكان تركيز الكادميوم في أوراق الكالبتوس أوراق الموجودة بن المطر و سرعة واتجاه الرياح التي أوراق الكالبتوس في النباتات الموجودة لي منطقة الدراسة ولوحظ انخفاض التركيز بين الفترتين بسبب الظروف الجوية خاصة سقوط المطر و سرعة واتجاه الرياح التي أوراق الكالبتوس أوراق الموجودة لي المول و المول و سرعة واتجاه الرياح التي أوراق الكالبتوس الفريان التي تم الحصول عليها. وكان تركيز الكادميوم في أوراق الكالبتوس الماخوذه من منطقة الدراسة فيتشرين الاول اعلى بالمقارنة مع قراءات العنصر أوراق الكالبتوس الماخوذه من منطقة الدراسة فيتشرين الاول اعلى بالمقارنة مع قراءات العنصر

كان معدل تركيز الهيدروكاربونات العطريه متعددة الحلقات المستخلصه من أوراق الكالبتوس في آذار (ppb٤٠,٣٤) وهو اعلى منه خلال شهر تشرين الاول (ppb٤٠,٣٤)، وهذا يرجع إلى انخفاض درجات حرارة الجو خلال الشتاء. حيث تمتص النباتات دائمة الخضره التراكيز العاليه من هذه المركبات.

استخدمت نظم المعلومات الجغرافية في هذه الدراسة لعمل الموديلات البيئيه من خلال ادخال نتائج التحليل الكيميائي للعناصر البيئية المختلفة (الهواء والتربة والنباتات) ضمن برنامج Arc GIS لبيان توزيع الملوثات في البيئة وتحديد المناطق الأكثر تاثرا بهذه الملوثات. وزارة التعليم العالي والبمث العلمي

جامعة بغداد

عمادة كلية العلوم



تغييم التأثيرات البيئية

لمحنى النغط في كركوك

أطروحة مقدمة إلى مجلس كلية العلوم - جامعة بغداد

وهي جزء من متطلبات نيل درجة دكتوراه فلسفة في علم الأرض / الصخور والمعادن

من قبل لمياء عبد الأمير علي ماجستير جيوكيمياء ١٩٩٥

بإشراف

الاستاذ د. معتز عبد الستار الدباس الخبيرد. عدنان حسن عفج ١٤٣٤