

An – Najah National University
Faculty of Graduate Studies

**Kinetics and Evaluation of Heavy Metals
and Nutrients in Leachates from
Fertilizers Using Soil Columns**

By

Sarah Mohammad Ahmad

Supervisor

Dr. Ahmad Abu-Obaid

Co-Supervisor

Prof. Shehdeh Jodeh

**This Thesis is Submitted in Partial Fulfillment of the Requirements for
the Degree of Master of Environmental Science, Faculty of Graduate
Studies, An-Najah National University, Nablus, Palestine.**

2016

**Kinetics and Evaluation of Heavy Metals and
Nutrients in Leachates from Fertilizers Using Soil
Columns**

By

Sarah Mohammad Ahmad

This thesis was defended successfully on 21/ 9/ 2016 and approved by:

Defense Committee Members

Signature

– Dr. Ahmad Abu-Obaid / Supervisor

.....

– Prof. Shehdeh Jodeh / Co-Supervisor

.....

– Dr. Ziad Shakhsher / External Examiner

.....

– Prof. Marwan Haddad / Internal Examiner

.....

III

Dedication

I dedicate this work to my family

Specially **my dad**

My **dear mother** “God bless her soul”

To **all my friends**

For Their support and encouragement throw out this Study.

With all my love and respect

Acknowledgement

I would like to thank my supervisor **Dr. Ahmad Abu-Obaid** for his supervision, encouragement and help throughout this study.

I would like also to thank my co-supervisor, **Prof. Dr Shehdeh Jodeh** For his valuable guidance and encouragement.

Special thanks to **Mr. Nafeth Dwekat** For his help with laboratory work involved in my research.

Thanks a lot to **Mr. Ibrahim Ghanam, Ms Sanaa Qasem and Ms Lubna Oweisat** for helping in this work.

Thanks to **my family** especially my father, who supported me throughout my study.

I also thank all of my friends and many people who helped in this work.

Sarah Mohammad

الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل عنوان

Kinetics and Evaluation of Heavy Metals and Nutrients in Leachates from Fertilizers Using Soil Columns

أقر أن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص باستثناء ما تمت الإشارة إليه حيثما ورد وإن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أية درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the Researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name:

اسم الطالبة: سارة محمد أحمد حسن

Signature:

التوقيع: سارة

Date:

التاريخ: 21/ 9/ 2016

Table of Contents

Dedication	III
Acknowledgement.....	IV
Declaration	V
Table of Contents	VI
List of Tables.....	VIII
List of Figures	IX
Abstract	XIII
Chapter One.....	1
Introduction:	2
1.1. General Introduction:	2
1.2. Objectives:	5
1.2.1. General Objective:	5
1.2.2. Specific Objectives:	5
1.3. Significance of Thesis:	6
Chapter Two.....	8
Literature Review.....	8
2.1. Introduction:.....	9
2.2. Characteristics of the soil:	9
2.2.1. Physical properties of soil:.....	10
2.2.2. Chemical properties of soil:.....	11
2.2.3. Chemical and physical properties of the soil controlling the heavy metals behavior and the availability of nutrients in the soil:	12
2.3. Nutrients and heavy metals:.....	16
2.3.1. Phosphorus (P):.....	16
2.3.2. Nitrogen (N):.....	18
2.3.3. Potassium (K):	19
2.3.4. Copper (Cu):	22
2.3.5. Iron (Fe):	24
2.3.6. Zinc (Zn):	25
2.3.7. Manganese (Mn):.....	27
2.4. Fertilizers:	29
2.5. Previous study:.....	33
2.6. Summary:.....	38
Chapter Three.....	40

3. Methodology:	41
3.1. Experimental Set up:	41
3.2. Experimental program:	41
3.2.1. Samples collection:	41
3.2.2. Soil Column Preparation:.....	42
3.2.3. Instrumentation:	45
3.2.4. Chemicals and Reagents:	46
3.3. Sample Digestion:	46
3.3.1. Digestion of fertilizer:.....	46
3.3.2. Digestion of soil:.....	47
3.4. Laboratory analysis:	47
3.4.1. Soil Analysis:	47
3.4.1.1. Soil Texture (Hydrometer Test):	47
3.4.1.2. Moisture (Water content):.....	48
3.4.1.3. Specific Gravity:	49
3.4.1.4. pH of Soil:.....	50
3.4.1.5. Organic Carbon:.....	50
3.4.2. Determination of Heavy Metals:.....	51
3.4.3. Determination of Nutrients:	51
3.4.3.1. Determination of Potassium:	51
3.4.3.2. Determination of Nitrogen:.....	52
3.4.3.3. Determination of Phosphorus:	54
Chapter Four.....	56
Results and Discussion:.....	57
4.1. Soil Tests:.....	57
4.2. Determination of the concentration of some Heavy Metals:	58
4.3. Determination of the concentration for some Nutrients:	79
4.4. Statistical Analysis:	94
Chapter Five	97
Conclusion and Recommendation:	98
1.5. Conclusions:.....	98
5.2. Recommendations:	99
Chapter Six.....	100
الملخص	ب

List of Tables

No.	Table	Page
Table (2.1)	Diameter and approximate size of four soil particles.	13
Table (2.2)	Average types and quantities of chemical fertilizers applied to irrigated crops in the west bank.	30
Table (2.3)	Target metals and concentrations standards (ppm) oven-dry soil, for pollution of soils in china.	34
Table (2.4)	Total metal concentrations in soil samples.	35
Table (2.5)	The concentration of some heavy metals in several samples of soil (ppm).	36
Table (4.1)	Specific gravity, moisture, texture, and pH for soil before pollution the soil.	57
Table (4.2)	Heavy metals concentrations in the 9 samples of soil, 10 samples of water which leachate from the soil fertilization, and one sample of compound fertilizer.	59
Table (4.3)	Nitrogen and Phosphoric concentrations in the 9 samples of soil, 10 samples of water which leachate from the soil fertilization, and one sample of compound fertilizer.	77
Table (4.4)	P- Value for Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3} in leachate water samples and fertilized/ unfertilized soil samples.	93
Table (4.5)	P- Value for NO_3^- , P_2O_5 and K_2O in leachate water samples and fertilized/ unfertilized soil samples.	94

List of Figures

No.	Figure	Page
Figure (2.1)	The four components of soil.	10
Figure (2.2)	Simplified representation of exchange, Because the colloid is primarily negatively charged, cations dominate the exchange sites.	11
Figure (2.3)	The pH scale.	14
Figure (2.4)	Relationships among readily available or exchangeable, unavailable and slowly available potassium in the soil plant system.	21
Figure (2.5)	The contrast of the concentration of some heavy metals in the study soil.	36
Figure (3.1)	Soil column apparatus.	42
Figure (3.2)	Soil column apparatus.	43
Figure (3.3)	cutting Soil column.	44
Figure (4.1.a)	Calibration curve of zinc (Zn^{+2}).	62
Figure (4.1.b)	plot of concentrations of zinc (Zn^{+2}) in leachate water samples.	62
Figure (4.1.c)	plot of concentrations of zinc (Zn^{+2}) in leachate blank water samples.	63
Figure (4.2.a)	plot of concentrations of zinc (Zn^{+2}) in fertilized soil samples.	64
Figure (4.2.b)	plot of concentrations of zinc (Zn^{+2}) in blank soil samples.	64
Figure (4.3.a)	Calibration curve of Manganese (Mn^{+2}).	65
Figure (4.3.b)	plot of concentrations of Manganese (Mn^{+2}) in leachate water samples.	66
Figure (4.3.c)	plot of concentrations of Manganese (Mn^{+2}) in leachate blank water samples.	66
Figure (4.4.a)	plot of concentrations of Manganese (Mn^{+2}) in fertilized soil samples.	67
Figure (4.4.b)	plot of concentrations of Manganese (Mn^{+2}) in blank soil samples.	67
Figure (4.5.a)	Calibration curve of Copper (Cu^{+2}).	68
Figure (4.5.b)	plot of concentrations of Copper (Cu^{+2}) in leachate water samples.	69
Figure (4.5.c)	plot of concentrations of Copper (Cu^{+2}) in leachate blank water samples.	69
Figure (4.6.a)	plot of concentrations of Copper (Cu^{+2}) in fertilized soil samples.	70
Figure (4.6.b)	plot of concentrations of Copper (Cu^{+2}) in blank	70

	soil samples.	
Figure (4.7.a)	Calibration curve of Iron (Fe^{+3}).	71
Figure (4.7.b)	plot of concentrations of Iron (Fe^{+3}) in leachate water samples.	72
Figure (4.7.c)	plot of concentration of Iron (Fe^{+3}) in leachate blank water samples.	72
Figure (4.8.a)	plot of concentration of Iron (Fe^{+3}) in fertilized soil samples.	73
Figure (4.8.b)	plot of concentration of Iron (Fe^{+3}) in blank soil samples.	73
Figure (4.9)	Histogram of Comparison of heavy metals concentrations (Zn^{+2} , Mn^{+2} , Cu^{+2} , and Fe^{+3}) in leachate blank and water samples.	75
Figure (4.10)	Histogram of Comparison of heavy metals concentrations (Zn^{+2} , Mn^{+2} , Cu^{+2} , and Fe^{+3}) in blank and fertilized soil samples.	77
Figure (4.11.a)	plot of concentrations of nitrate (NO_3^-) in leachate water samples.	81
Figure (4.11.b)	plot of concentrations of nitrate (NO_3^-) in leachate blank water samples.	81
Figure (4.12.a)	Calibration curve of nitrate (NO_3^-) at 410 nm.	82
Figure (4.12.b)	plot of concentrations of nitrate (NO_3^-) in fertilized soil samples.	83
Figure (4.12.c)	plot of concentrations of nitrate (NO_3^-) in blank soil samples.	83
Figure (4.13.a)	Calibration curve of phosphorus as P_2O_5 at 840 nm.	84
Figure (4.13.b)	plot of concentrations of Phosphorus as P_2O_5 in leachate water samples.	85
Figure (4.13.c)	plot of concentrations of Phosphorus as P_2O_5 in leachate blank water samples.	85
Figure (4.14.a)	plot of concentrations of Phosphorus as P_2O_5 in fertilized soil samples.	86
Figure (4.14.b)	plot of concentrations of Phosphorus as P_2O_5 in blank soil samples.	86
Figure (4.15.a)	calibration curve of potassium as K_2O at 234 nm.	87
Figure (4.15.b)	calibration curve of potassium as K_2O at 234 nm.	88
Figure (4.16.a)	plot of concentrations of Potassium as K_2O in leachate water samples.	88
Figure (4.16.b)	plot of concentrations of Potassium as K_2O in leachate blank water samples.	89

Figure (4.17.a)	plot of concentrations of potassium as K_2O in fertilized soil samples.	89
Figure (4.17.b)	plot of concentrations of potassium as K_2O in blank soil samples.	90
Figure (4.18.a)	Histogram of Comparison of the nutrients concentrations (NO_3^- , P_2O_5 and K_2O) in leachate blank and water samples.	91
Figure (4.18.b)	Histogram of Comparison of the nutrients concentrations(NO_3^- , P_2O_5 and K_2O) in blank and fertilized soil samples.	93

List of Abbreviations

Symbol	Abbreviation
11 (water leachate)	Leachat water Sample 1 from fertilized column 1 after 1 day.
12 (water leachate)	Leachat water Sample 2 from fertilized column 1 after 5 days.
13 (water leachate)	Leachat water Sample 3 from fertilized column 1 after 10 days.
14 (water leachate)	Leachat water Sample 4 from fertilized column 1 after 20 days.
15 (water leachate)	Leachat water Sample 5 from fertilized column 1 after 30 days.
21 (blank) (water leachate)	Leachat water Sample 1 from blank column 2 after 1 day.
22 (blank) (water leachate)	Leachat water Sample 2 from blank column 2 after 5 days.
23 (blank) (water leachate)	Leachat water Sample 3 from blank column 2 after 10 days.
24 (blank) (water leachate)	Leachat water Sample 4 from blank column 2 after 20 days.
25 (blank) (water leachate)	Leachat water Sample 5 from blank column 2 after 30 days.
1A0 (soil)	Sample 1 from fertilized column 1, at 0 cm height.
1AB45 (soil)	Sample 2 from fertilized column 1, at 45cm height.
1BC90 (soil)	Sample 3 from fertilized column 1, at 90 cm height.
1C135 (soil)	Sample 4 from fertilized column 1, at 135cm height.
2A0 (blank) (soil)	Sample 1 from blank column 2, at 0 cm height.
2AB45 (blank) (soil)	Sample 1 from blank column 2, at 45 cm height.
2 BC90 (blank) (soil)	Sample 1 from blank column 2, at 90 cm height.
2 C135 (blank) (soil)	Sample 1 from blank column 2, at 135 cm height.

**Kinetics and Evaluation of Heavy Metals and Nutrients in Leachates
from Fertilizers Using Soil Columns**

By

Sarah Mohammad Ahmad**Supervisor****Dr. Ahmad Abu-Obaid****Co-Supervisor****Prof. Shehdeh Jodeh****Abstract**

Since there was no data about heavy metals content in fertilizers used in Palestine, this study could provide useful new data for the Ministry of Agriculture in Palestine. Measured levels of heavy metals in fertilizer show further information about their rate in fertilizers.

Heavy metals: zinc (Zn^{+2}), manganese (Mn^{+2}), copper (Cu^{+2}) and iron (Fe^{+3}) concentrations that leached out from fertilizers were determined by using flame atomic absorption spectrophotometer (AAS). In addition to that, some nutrients: phosphorus as P_2O_5 , potassium as K_2O , and nitrogen as NO_3^- concentrations were determined by using two methods. The first method was ultraviolet visible (UV-VIS) method, which was used for the analysis of phosphorus as P_2O_5 , nitrogen as NO_3^- (in soil samples and one sample of compound fertilizer), and potassium as K_2O . The second method was photometer nitrate instrument, which was used for the analysis of nitrogen as NO_3^- in ten water samples. One sample of agricultural red soil from Nablus and one sample of compound fertilizer 20/20/20 (N/ P/ K) used in Palestine were both taken. Statistical analysis and figures were used to help understand the processes occurring in soil.

The results indicate that compound fertilizer 20/20/20, which is used in Palestine, is a main source for many heavy metal pollutants and nutrients.

Linear Regression Statistical test show that there is a significant variation, in the concentration of the heavy metals and nutrients in samples of fertilized soil and leachate water samples. So it can pollute the environment by the accumulation of heavy metals such as Cu^{+2} , Mn^{+2} , Fe^{+3} and Zn^{+2} in addition to nutrients such as P_2O_5 and K_2O on the surface of the soil. It can also leach to the ground water and pollute it with NO_3^- , Fe^{+3} , Mn^{+2} and Zn^{+2} . Thus, these results suggest that the fertilized soil with compound fertilizer 20/20/20 is rich with various toxic heavy metals particularly Cu^{+2} , Mn^{+2} and Zn^{+2} , as well as other nutrients, particularly NO_3^- which causes ground water pollution.

Chapter One

Introduction

Introduction:

1.1. General Introduction:

Soil is the top layer of solid crust, which can be defined as a varied component of organic constituents and minerals, (**Ayoub et al., 2003**). Soil is a natural body that varies in chemical properties, constitution, physical properties, composition, and biological characteristics, (**Ronald, 1994**).

Soil consists of 13 to 16 essential elements that are important for plant growth, (**Zaher et al., 2012**). Plants take oxygen, carbon, and hydrogen from air and water, as well as energy from the sun. Other nutrients are taken from the soil. These nutrients are divided into two types: macronutrients and micronutrients. Macronutrients are the main nutrients which are divided into primary and secondary. The primary nutrients that are predominantly required for the plant are, potassium (K), nitrogen (N), and phosphorous (P). Secondary nutrients are calcium (Ca), magnesium (Mg), and sulfur (S). Micronutrients are boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn).

Plants consume nutrients from the soil to grow. This consumption depends on the type of cultivated crops. For example, corn consumes nitrogen from the soil more than legumes, because legumes have the ability to fix nitrogen from air. Nutrients must be replaced when they are depleted by plants to maintain soil fertility. The fertility of soil increases by adding fertilizers.

Fertilization plays an important role in plant development, (**Clark and Kelly, 2004**). It provides it with the nutrients that are essential for its growth, (**International Fertilizer Development Center, 2001**). Therefore, fertilized soil produces agricultural crops better than the agricultural crops of unfertilized soil.

Fertilizers are important elements of food production worldwide. As population grows, agricultural land requirements increase, as a result more fertilizers play a major role to accommodate with this expansion. For instance, agriculture is widely dependent on the use of fertilizers to increase fertility of soil, to increase crop production, and to compensate the nutrients that the soil is deficient of. (**Clark and Kelly, 2004**).

The world cannot provide its food production goals without improved genetics, biotechnology and fertilizers, (**Roberts, 2009**). Since 1900s, application of fertilizers grew significantly and continued for the being time in different countries. Asia is the largest commonly user of fertilizers in the world. More than 50% of fertilizers are expected to be consumed by Asia in the period of 2000 and 2030.

Two kinds of fertilizers are used to increase the soil fertility, matter fertilizers (animal manure) and chemical fertilizers. These fertilizers contain the nutrients that are needed for plants development.

Matter fertilizers consist of organic wastes that are added into soil. Organic wastes as compost, sewage sludge, animal manure, crop remnant, and bone meal. In the 19th century, the usage of chemical fertilizers began. (**International Fertilizer Development Center, 2001**); (**Clark and Kelly,**

2004). Inorganic fertilizers are commercial fertilizers that consist of chemical substances. The main nutrients of inorganic fertilizers are phosphorus, potassium, and nitrogen, while secondary nutrients include Mg, S, and Ca. Inorganic fertilizers also contain micronutrients such as Na, Mo, Zn and Fe. Nutrients of inorganic fertilizers are different according to the type of crops and soil, (**International Fertilizer Development Center, 2001**); (**Mohamed, 2012**). The percentage of inorganic fertilizers for world's food production is about 40 to 60%. (**Roberts, 2009**).

The percentage of organic fertilizers in Palestine in 2010 is 64.9% and 34.8% for inorganic fertilizer, (**Palestinian Central Bureau of Statistics, 2012**). Inorganic fertilizers add more nutrients to the soil per unit weight than organic fertilizers. Organic fertilizers are considered eco-friendly for the environment, while inorganic fertilizers are not. (**Clark and Kelly, 2004**).

Inorganic fertilizers do not only contain the main nutrient and micronutrients, they also contain traces of pollutant heavy metals such as Pb, As, and Cd that cause soil toxicity when they are used for long term, (**Mohamed, 2012**); (**Ajayi et al., 2012**). Heavy metals in fertilizers threaten the soil farming and environment. Some heavy metals are toxic to plants themselves. Plants absorb some heavy metals and keep them in their tissues. Existence of heavy metals in these fertilizers means that they may contain prohibited substances and ingredients. (**Diana and Brian, 2003**).

The presence of heavy metals in soil is one of the most important environmental problems throughout the world. (**Dube et al., 2001**).

Accumulation of heavy metals in large quantities in the soil is toxic to humans and animals. Through food chain transfer, humans are exposed to heavy metals which cause chronic effect. For example, arsenic and cadmium affect kidneys, arsenic affects the central nervous system and causes skin poisoning, while cadmium affects liver and gastrointestinal tract. (**United States Department of Agriculture, 2000**); (**Omama et al., 2015**).

Inorganic fertilizers threaten the safety of food in the world, (**Roberts, 2009**). For example when inorganic fertilizers are applied in excess they affect coastal water ecosystems, (**Raven and Taylor, 2003**). Also, they increase greenhouse gas emissions as nitrous oxide (N_2O). (**Matson et al., 1998**).

1.2. Objectives:

1.2.1. General Objective:

The main objective of this project is to determine the concentration of heavy metals and nutrients that leached out from one type of fertilizers in Palestine, using the idea of soil columns made from poly vinyl chloride (PVC).

1.2.2. Specific Objectives:

1. To determine the concentration of some heavy metals (Cu^{+2} , Mn^{+2} , Fe^{+3} and Zn^{+2}) that leached out from 20/ 20/ 20 (N/ P/ K) compound fertilizer in Palestine.
2. To determine the concentration of some heavy metals (Cu^{+2} , Mn^{+2} , Fe^{+3} and Zn^{+2}) in several samples of red soil in Palestine.

3. To determine the concentration of some nutrients such as P_2O_5 , NO_3^- and K_2O in 20/ 20/ 20 (N/ P/ K) compound fertilizer, and their leachate in several samples of red soil in Palestine.
4. To determine some physical and chemical properties of one type of red soil.

1.3. Significance of Thesis:

The increase in food production due to growing world population requires the agricultural crops to depend on the consumption of large quantities of chemical fertilizers.

Chemical fertilizers that contain nutrients and heavy metals such as Fe^{+3} , Mn^{+2} , Cu^{+2} , and, Zn^{+2} are widely used in the world. The use of chemical fertilizers continuously by several countries, leads to the accumulation of heavy metals in the soil, which causes atmospheric contamination. Because of the risks resulting from this problem, they receive increasing attention from environmental organizations, and public policy makers.

Palestine is one of the developing countries which uses tons of chemical fertilizers annually. This is the first study on the effect of chemical fertilizers and its nutrients on the red soil of Palestine. This study also focuses on the environmental risks of metal leaching and ground water contamination by these metals, resulting in the accumulation of heavy metals in the soil of Palestine.

Red soil was selected because it is one of the most soil types used by farmers in Nablus. It contains at least 40% clay, less than 40% silt, and less than 45% sand. It also contains nutrients that plants need for growth,

the small pores and small space between the particles of red soil give it the ability to retain water, making it a good soil for agriculture.

Heavy metals Zn^{+2} , Cu^{+2} , Mn^{+2} and Fe^{+3} were selected because of the risks resulting from them. They may accumulate on the surface of the soil and form toxic compounds. They also may leach to ground water and pollute the environment.

Chapter Two
Literature Review

2.1. Introduction:

Every year large quantities of chemical fertilizers are sold and consumed in Palestine and worldwide, to compensate the soil for the lack of nutrients by the plants. These chemical fertilizers not only contain the essential nutrients for plants, but also contain specific amounts of trace elements and heavy metals.

According to Palestinian central statistics, the percentage of chemical fertilizers used in Palestine is 34.8%, (**Palestinian Central Bureau of Statistics, 2012**). This percentage is expected to increase in the following years. The use of these chemical fertilizers in large quantities leaves a lot of adverse effects on the environment. When the nutrients and heavy metals accumulate in the soil, it becomes polluted. Also, when the pollutants leach in the soil, it pollutes the ground water and threatens human life, (**Tomoyuki and Yongming, 2010**). One type of fertilizer was selected for this study, which is a compound fertilizer 20/20/20 because of its large use. The concentration of some nutrients and heavy metals in fertilizers and samples of clay soil and leaches were measured.

2.2. Characteristics of the soil:

Soil is an important component of environments. Plants are capable of absorbing many nutrients (forty or fifty chemical elements) from soil, sixteen of them are essential to the growth of most plants. These nutrients determine the capacity of soils to be productive. As the concentration of nutrient in the soil decreases, the amount of nutrients which will be

required for the soil to increase crop productivity increases. Soil characteristics (the chemical, physical, and biological characteristics of a soil as texture, organic matter content, acidity, water retention capacity, and depth) influence fertility of soil. (Peter et al., 2000); (Joan, 1999).

2.2.1. Physical properties of soil:

Soil consists of a mixture of organic matter, air, minerals, and water. Figure (2.1). The physical composition and proportion of the previous components are the most important features that influence soil physical properties, such as the fraction of pore space in a soil (water and air), texture, and structure. (Ann et al., 2005); (Smith et al., 1928).

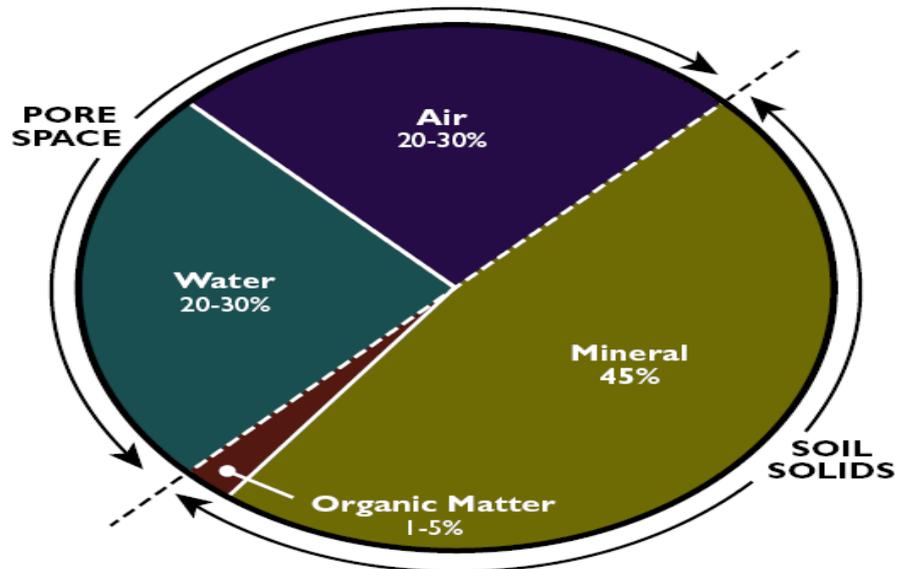


Figure (2.1): The four components of soil. Organic matter and minerals make up the solid fraction, whereas water and air comprise the pore space fraction. A typical agricultural soil is usually around 50% solid particles and 50% pores (Brady and Weil, 2002).

2.2.2. Chemical properties of soil:

Knowing the chemical properties of the soil such as soil pH, essential nutrients, water and organic matter are important to the success of growth of all plant life, (Joan, 1999). Because of the charge of colloid surfaces of the soil, most chemical interactions occur on it. Colloid surfaces have the ability to attract or sorb ions within the soil solution, because of the large surface area of it. Factors that control the ions (for held and sorbed to the colloid surface or exchanged with other ions then released to the soil solution) are the size of ions, concentration in the soil and charge. The ‘exchange capacity’ of the soil (ability to exchange and sorb ions) is shown in figure 2.2 (Brady and Weil, 2002).

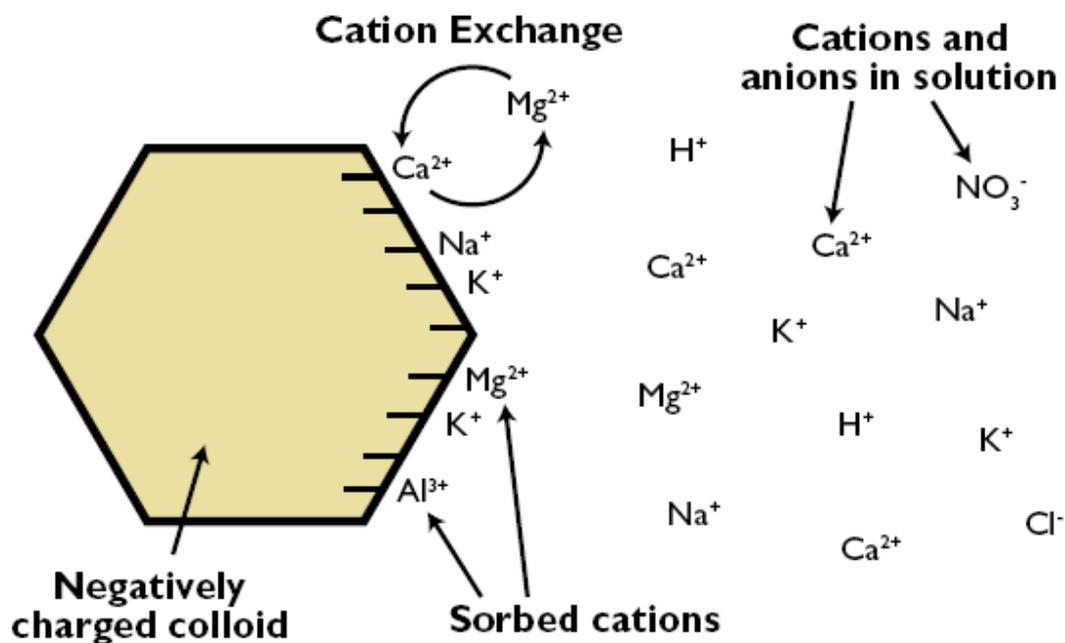


Figure (2.2): Simplified representation of exchange capacity. Because the colloid is primarily negatively charged, cations dominate the exchange sites (Brady and Weil, 2002).

All soils contain amounts of heavy metals or trace elements such as iron (Fe^{+3}), zinc (Zn^{+2}), manganese (Mn^{+2}) and copper (Cu^{+2}), which are essential for plants, (**Brian, 2008**). There are many chemical and physical characteristics of the soil controlling the heavy metals behavior. (**Laing et al., 2007**); (**Clark and Kelly, 2004**).

2.2.3. Chemical and physical properties of the soil controlling the heavy metals behavior and the availability of nutrients in the soil:

2.2.3.1. Depth:

The groundwater depth is an important factor because by knowing it, we can determine the volume of soil that contaminants need to move in before reaching an aquifer. If the soil is shallow, it can absorb a specific amount of pollutants leading to potential pollution on the surface. Conversely, if the soil is deep, the following process occurs effectively as filtration, sorption, volatilization and biodegradation. (**Osama et al., 2011**).

2.2.3.2. Texture:

Texture is one of the most important physical properties of soil. The texture depends upon the relative proportions of three mineral particles, such as silt, clay and sand. These particles are characterized by their fine mineral fraction and size as indicated in table 2.1, (**Brady and Weil, 2002**); (**Smith et al., 1928**). Based on the size of soil particles, there are three types of soil: silt, clay and sand.

Table (2.1): Diameter and approximate size of three soil particles
(Brady and Weil, 2002).

Soil Particle	Diameter (mm)	Approximate Size
Sand	0.05-2.0	●
Silt	0.002-0.05	•
Clay	<0.002	Invisible to naked eye

Clay soil is one type of soil that contains at least 40% clay, less than 40% slit and less than 45% sand. Clay soil has small pores and small space between the particles, so the soil tends to bond together strongly. Clay soil has a negatively charged large surface area, on which sorption can take place. While sandy soil is one type of soil that contains at least 85% sand, the remaining percentage is clay and slit, but the percent of clay is more. Sandy soil has low surface area, large pores and space between the particles, allowing water to percolate through the soil rapidly. Slit soil is one type of soil that contains at least 80% or more slit and less than 12% clay. Slit soil has medium pores and spaces between the particles, as a result, leaching through the soil is more in sandy soil and less in clay soil. **(Joan,1999); (Osama et al., 2011); (Zaher et al., 2012).**

Soil texture plays an important role in the ability to exchange materials that are transported in the solution, **(Perk, 2007)**. The nature of the texture of the soil is very important because it determines the amount of nutrients such as nitrate ions that are held in the soil. Clay soil has a major effect on the leaching of nitrate, because of the negatively charged surface, the

nitrate is not attracted to the surface of it. So it stays in the soil solution. (Osama et al., 2011).

2.2.3.3. Organic Matter Content:

Organic matter content is described quantitatively by the organic level of carbon in the soil. Organic matter content is important for several things as it enhances the absorption and release of nutrients; it also helps plants grow by improving drought-resistance and water-holding capacity. It is quite effective in retaining metals and humus matter. Also, it is important for the proper management of soil fertility, and it makes the soil less susceptible to erosion and leaching. (Peter, 2000); (Silveira. et al., 2003).

2.2.3.4. Soil pH:

The pH of a soil is one of the most important physical properties that influence the reactions in a soil and affecting soil fertility. It has a great importance to microbial activity and plant roots, as it is an indicator to a soil's acidity and basicity (alkalinity). (Michael, 2006); (Henry and Boyd, 1988); (Clark and Kelly, 2004).

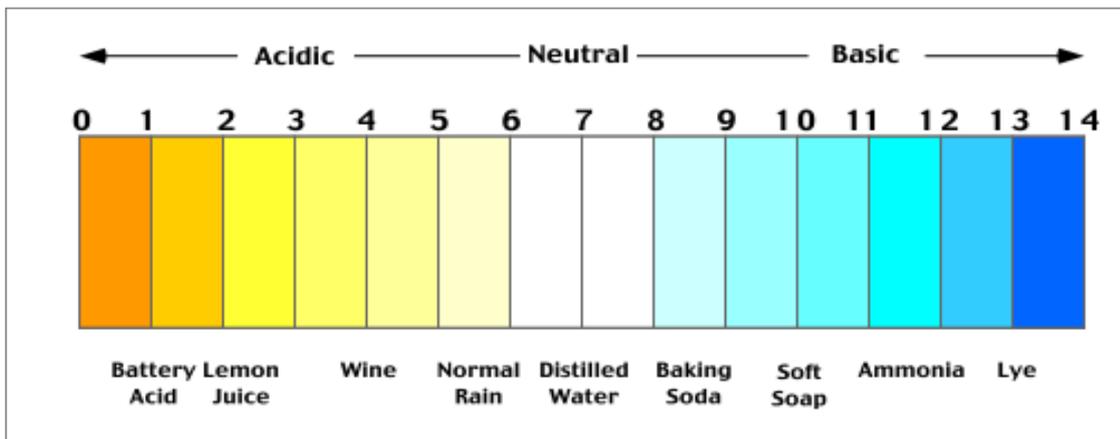


Figure (2.3): The pH scale, (Source: Michael, 2006)

The pH of most soils is within the range of 4 to 10, (**Henry and Boyd, 1988**). If the pH of the soil is extreme, either acid or alkaline or neutral, the plant will die, (**Shaima and Ayat , 2011**). Soils with pH values outside the previous ranges are normally toxic to most plants. For instance, in very strongly acidic soils the concentrations of toxic metals in the soil solution will rise, which negatively affects the plants. (**Joan, 1999**).

The pH is a key factor for the availability of plant micronutrients in the soil, as it influences the fertility of the soil through its control of the solubility of many nutrients. At higher pH, the availability of nutrients are decreased, because the nutrients become insoluble and the plants cannot take them in easily. In contrast, at pH lower than 5.5 many nutrients become soluble and available to the plant and may leach from the soil to the groundwater. In most cases, the maximum soil fertility is at a pH in the range of about 6-7.5, allowing optimal solubility, especially for the primary nutrients of potassium, phosphorous and nitrogen. (**Osama et al., 2011**); (**Clark and Kelly, 2004**).

The pH plays an important role in the mobility of nutrients as heavy metals in the soil. The ability of soil to hold the metals on the soil surface through absorption process increase as the pH increases, (**Appel et al., 2002**), but as the value of pH decreases, the solubility of trace elements in the soil increases. (**Bang et al., 2004**).

The variation of pH has an effect on the exchangeable cation in acid soils. This effect results in poor for adsorption of the monovalent hydrogen on

the exchange sites of clays. On the acidic groups of the organic matter, some H⁺ ions are adsorbed. **(Henry and Boyd, 1988).**

2.3. Nutrients and heavy metals:

2.3.1. Phosphorus (P):

Phosphorus is a major element that can be found in all living organisms, **(Syers et al., 2008); (Andrew et al., 1914)**. It is one of the three primary nutrients for plants that they absorb by roots. Phosphorus constitutes about 0.2 fraction of the plants' weight. Although a small amount, it is critically important, **(Charles et al., 2005)**. Phosphorus plays a major role in many physiological and biochemical processes. **(Syers et al., 2008)**.

Phosphorus is an important element in plants, since it is necessary for many life processes such as metabolism of carbohydrates and photosynthesis, as well as processes that require a transfer of energy, like the formation of fats, **(Joan,1999)**. It is also necessary for producing a strong root system and healthy rhizome, along with the development of reproductive parts and DNA formation. Phosphorus is an indispensable element. It is considered a structural component, as it is a component of phospholipids, adenosine triphosphate (ATP), nucleic acids, sugar phosphates and more. It influences the general vegetative growth for plants. **(Syers et al., 2008); (Charles et al., 2005)**.

Phosphorus deficiency symptoms in plants are: small leaf size, reduced flower development, low seed quality, the leaves appears dark bluish green, and decreased crop yield. The characteristic visual symptom of phosphate

deficiency is widespread chlorosis of the leaves. **(Schulte and Kelling, 1996); (Charles et al., 2005).**

Phosphate fertilization is especially necessary, in order to solve the problem of lack or deficiency of phosphorus in the soil, which affects the growth of plants. However, it can be harmful to the environment when put in large amounts in soil, **(Charles, et al., 2005)**. Since 200 years ago phosphate fertilizer has been put in the soil, to compensate for shortage of phosphorus, to produce suitable yields of crops, meeting the need of an increasing population, **(Syers et al., 2008)**.

Phosphorus, unlike some other elements, reacts with soil constituents to form insoluble compounds that are immobile in soil. It is held on the surfaces or within soil components, so it is not leached from the soil. It is usually adsorbed initially, then it is converted by growing plants into organic form which tends to accumulate in the surface of soil in plants. For this reason, there is little possibility that groundwater would become polluted from the use of phosphorus fertilizer. **(Smith et al., 1928); (Foth and Turk, 1972); (Syers et al., 2008)**.

Phosphorus exists in four general forms in soil: (1) inorganic phosphorus (2) organic phosphorus, (3) adsorbed phosphorus, and (4) primary mineral phosphorus. Plant roots absorb phosphorus from the soil as orthophosphate ions, principally H_2PO_4^- and a few as HPO_4^{2-} . **(Charles et al., 2005)**.

2.3.2. Nitrogen (N):

Nitrogen is one of the essential element nutrients needed for all living organisms, it is also one of the most abundant elements in the universe, and the most important nutrient for plants. It also comprises about 78% (4,000 trillion tons) of the gas in the atmosphere. **(Zaher et al., 2012); (James, 2013).**

Nitrogen is the nutrient required in the largest amounts for plants. It enters in the installation of organic molecules as all proteins including enzymes, nucleic acids and amino acids. It is also important for chlorophyll buildup associated with the photosynthetic activity. The availability of nitrogen is closely associated with plant productivity. The plant's utilization of other major elements is stimulated by the presence of nitrogen. Nitrogen also stimulates above-ground growth and produces the rich green color that is characteristic of a healthy plant. **(James, 2013); (Zaher et al., 2012); (Joan, 1999).**

Nitrogen deficiency symptoms in the plants are: yellow or dark green leaves and stunts in growth, **(Henry and Boyd, 1988)**. Consumption of nitrogen by plants leads to leaching of the nitrogen in the soil. Nitrogen fertilizers will be used, where necessary, to increase the nitrogen in the soil. If application of nitrogen fertilizers to the soil is excessive, then the excess nitrate cannot be taken up by the plant, but it leaches into groundwater and contaminates wells. **(Osama et al., 2011).**

Excessive use of nitrogen fertilizers threat not only the environment, but also the agricultural itself, **(Johennes, 2013)**, so there is a negative impact

of using nitrogen fertilizers in large quantities, (**Osama et., 2011**). In addition to leaching, most nitrogen fertilizers cause soil humus depletion, greenhouse gas emissions and soil acidification which are big contributors to climate change. This causes harmful effects to the climate and soil. (**Johannes Kotschi, 2013**).

Plants take Nitrogen in two forms: nitrate (NO_3^-) and ammonium (NH_4^+). The nitrate is more available for plants than ammonium, (**Zaher et al., 2012**); (**James Walworth, 2013**), but because the solubility of nitrate is high, this may allow nitrates to pass to groundwater, which leads to a dangerously high concentration of nitrates in groundwater. The standard of nitrate ion concentration is 45 mg/L by the World Health Organization (WHO). (**Osama et al., 2011**).

One of the important factors that affect the interaction of nitrogen in the soil is organic matter. Organic matter is sufficiently rich in nitrogen. The degradation of organic matter releases nitrate nitrogen and ammonium by a process called mineralization. (**James, 2013**).

2.3.3. Potassium (K):

Potassium is considered to be one of the very important macronutrient materials, which is needed for plant growth and development in most agricultural crops, by being absorbed from the root zone through diffusion. (**Zaher et al., 2012**); (**George and Michael, 1997**).

In fact, potassium is very essential for vitality and vigor of the plant, and it is included in many physiological activities in the plant cell as well as in

the coordination between tissues and organs in the whole plant. It can help the roots to be healthy by avoiding the bad effects of excessive nitrogen in the soil that affect on pre-maturity of the plant, because it plays an important role in balancing the effect of excessive nitrogen levels. Moreover, potassium regulates the transport rate via regulating stomatal movement, by maintaining electro-neutrality in plant cells, where a high transpiration rate increases nutrient absorption. Potassium also is responsible for the synthesis of starch, the translocation of carbohydrates, synthesis of proteins, normal cell division, and growth in the plant. Adequate amounts of potassium can increase the protein production, improve efficiency of photosynthesis, stimulate early growth, increase resistance of the plant to insects and some diseases, and results in greater water uptake efficiency. **(Joan, 1999); (George and Michael, 1997); (Ross, 2013).**

Since potassium is the most abundant in the earth's crust compared with other nutrients, it is supplied naturally in the soil, but sometimes the quantity of it is not enough for the growth of the plants. Therefore, the soil supply of potassium must be added by fertilization, other wise growth will stop and crop production will be reduced. **(George and Michael, 1997); (Henry and Boyd, 1988).**

Three forms of potassium exist in the soil, **(Ross, 2013)**, which are: readily available, the unavailable, and slowly available. The following figure (2.4) illustrates these forms. **(George and Michael, 1997).**

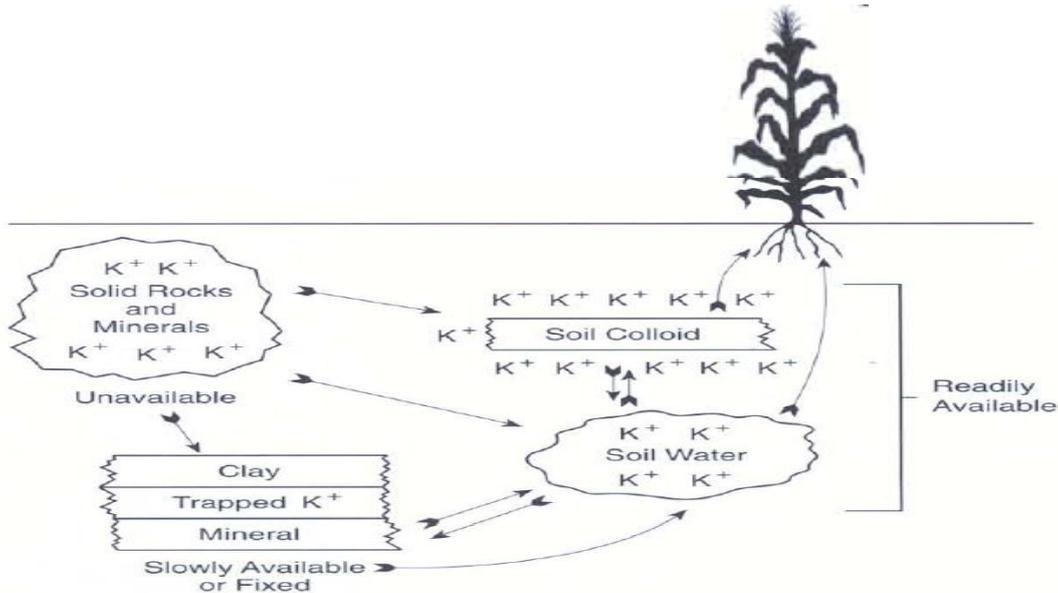


Figure (2.4): Relationships among readily available or exchangeable, unavailable and slowly available potassium in the soil-plant system (George and Michael, 1997).

Movement of Soil Potassium:

Because clay and organic matter particles hold potassium ions in a readily available potassium pool, potassium does not leach from slity or clayey soils. The concentration of potassium in the soil solution and the amount of water that leaches through the soil are the measure factors that control the loss of potassium by leaching. Some leaching might increase as soils become more sandy, because there is not enough clay in sandy soils to hold the potassium. Therefore the attraction between organic matter particles and potassium is relatively weak in sandy soil.

Potassium in soil solution and in exchangeable form occurs as a positively charged ion, (K^+). Soil colloids and the surface of soil clay minerals are negatively charged. Organic matter particles hold most positively charged nutrients tightly. Potassium will tend to be adsorbed onto the surface of soil particles. As a result, soil potassium is not subject to leaching or downward

movement in slity or clayey soils. **(Henry and Boyd, 1988); (Schulte and Kelling, 1914).**

Plants take up potassium in ionic form as K^+ , **(Ross, 2013)**. The plants need a daily amount of potassium, leading to deficiency in the soil, **(Henry and Boyd, 1988)**. These deficiencies can be compensated by potassium fertilizer as K_2O . **(Ross, 2013)**.

2.3.4. Copper (Cu):

Copper is a transition metal, and it is an essential micronutrient. In addition, it is the third essential element used in the world, and it is required in the growth of both animals and plants. **(Diana and Brian, 2003); (Kareem et al., 2010)**.

Copper plays an important role in humans and plants, as it helps in the production of blood hemoglobin in humans. In plants, copper plays an active role in seed production, and anaerobic metabolism. Cu-proteins have been implicated in lignifications. They also exhibit electron transfer and oxidizing activity. Copper proteins also play an important role in the regulation of water, hormonal metabolism, and are a critical component in some enzymes performing key functions as photosynthesis and respiration.

Copper is a very essential element, but increasing the concentration of it has negative effects. In humans it can cause intestinal irritation, deposits in the eyes, brain, skin, stomach irritation and kidney damage, **(Kareem et al., 2010)**. Large doses of copper more than 100 mg are harmful to humans, and can cause failure of pigmentation of hair, central nervous system disorder, and liver damage. **(Mohammed et al., 2002)**.

Copper deficiency symptoms in plants are in the form of leaf rosettes, distorted leaves, stopped growth, and pale yellow-white leaves. Copper fertilizers will also be used, where necessary, to increase the copper in the soil. Excessive application of copper fertilizers leads to copper accumulation in soil. Copper needs to be restricted in fertilizers in order to properly monitor and prevent copper accumulation, **(Diana and Brian, 2003)**. The increase of copper concentration in the environment does not pose a risk because it is different from the other elements; it is not a cumulative systemic poison, because it rapidly becomes stable. **(Kareem et al., 2010); (Mohammed et al., 2002)**.

Copper exists in the soil as a cation (Cu^{+2}) form. The main factors controlling the availability of copper in the soil are: pH of the soil and organic matter.

1. pH of the soil: at pH 5.5 the solubility of Cu is dramatically increased. Also the copper availability decreases as the pH increases. **(Kareem et al., 2010)**.
2. Organic matter: as organic matter in soil increases, copper availability decreases. (Cu^{+2}) cation is held strongly by adsorption on surfaces of clay minerals or with organic matter, **(Kareem et al., 2010); (Henry and Boyd, 1988)**. Organic matter binds copper more tightly than other micronutrients, this decreases the leaching of it in the soil. Sufficient copper is released to support normal crop growth after the organic matter begins to decompose. **(Schulte and Kelling, 2004)**.

2.3.5. Iron (Fe):

In 1845, iron was considered to be an essential element, and generally recognized as a plant micronutrient. Iron is an important metal that is essential for plant growth. It is absorbed by plants as the ferrous ion Fe^{+2} , plants regulate iron uptake.

Iron is essential for plant growth because it plays an important role in plant biochemistry as in the formation of chlorophyll, energy transformation, functions in some of the enzymes of the plants, and is implicated in nucleic acid metabolism. It occurs in heme and nonheme proteins, and plays a role in the mechanisms of photosynthetic electron transfer. Nonheme iron proteins are involved in the reduction of nitrates and sulfates.

Iron deficiency symptoms in the plants are: yellowing of immature leaves, the less green (or yellow) tissue between veins, Fruits tend to be pale-yellow rather than green-yellow. Because iron is relatively immobile inside the plant, the younger leaves are more affected than older leaves. **(Environmental Protection Agency, 2003).**

Iron is an abundant element present in soil and rocks. Iron exists in more than one oxidation state in the soil: namely Fe^{+2} , Fe^{+3} , Fe^{+} .

If the soil minerals do not gradually release ferrous (Fe^{+2}) iron to replace that which is being oxidized to ferric iron over time, iron deficiencies may result. The deficiency of iron in soil can be treated with iron fertilizers in specific amounts. (Fe^{+3}) iron accumulates in highly weathered soils and is a major constituent of the red soils. This problem is associated with the extremely insoluble nature of certain compounds of ferric (Fe^{+3}) iron.

There are several soil conditions that influence on iron availability to plants, which include: pH, soil moisture, and organic matter content.

1. pH: as soil pH increases, the availability of iron in soil solution to plants decreases, and iron oxides can precipitate on clay surfaces.
2. Organic matter: as organic matter increases the availability of iron in soil solution to plants increases, while as organic matter decreases the availability of iron in soil solution to plants decreases. **(Henry and Boyd, 1988); (Environmental Protection Agency, 2003).**

2.3.6. Zinc (Zn):

Zinc is a transition metal, and it is an essential micronutrient. It is one of the eight trace elements (iron, boron, nickel, manganese, molybdenum, chlorine, and copper).

Zinc is essential for particular physiological functions in humans, animals and plants as facilitation of the largest number of protein synthesis and enzymes. It binds with more than 300 enzymes and 925 different proteins in humans. It also has a role in the maintenance of structural and functional integrity of biological membranes in many important biochemical pathways. Zinc plays a key role in plants, therefore an adequate zinc intake is important for reproduction of crop plants and the normal healthy growth of higher plants.

A specific amount of zinc is required to regulate and maintain the expression of genes needed to protect cells and allows them to tolerate environmental stress conditions. **(Brian, 2008).**

Zinc deficiency symptoms in plants are: poor plant growth which adversely affects and the quality of crop products, because one or more of the many important physiological functions of zinc is unable to operate normally, such as by the dysfunction of several enzyme systems and other metabolic functions in which zinc plays a part. The changes in plant physiological mechanisms include one or more of the following: small and abnormally shaped leaves, stunting (reduced height), bronzing of chlorotic leaves, and interveinal chlorosis (yellowing of the leaves between the veins), these symptoms vary with plant species. **(Brian, 2008)**.

The problem of zinc deficiency is therefore a global one because zinc is the most important metal of all of the previous eight metals. Zinc fertilizers will also be used, where necessary, to increase the zinc in the soil. Excessive application of zinc fertilizers lead to zinc accumulation in the soil to possibly harmful levels, which can be toxic to plants. This is unlikely in most agricultural systems, **(Brian, 2008); (Diana and Brian, 2003)**. In addition to that, water-soluble zinc that is located in soils can contaminate groundwater and cause health problems. **(Raymond and Felix, 2011)**.

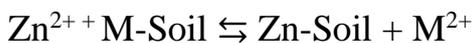
Zinc will exist in more than one form in the soil: the water soluble form, adsorbed and exchangeable form, and insoluble form. **(Brian, 2008)**.

The main factors controlling the interaction of zinc in the soil are:

The pH of the soil (as the pH increases the solubility of zinc decreases), **(Henry and Boyd, 1988)**, the concentration of Zn^{2+} in the soil solution, the concentration of all ligands capable of forming organo-zinc complexes,

weather conditions (**Schulte and Killing, 2004**), and the type and amount of adsorption sites associated with the solid phase of the soil.

Knowledge of the dynamics of Zn in soils is important and it enables us to understand the transport and uptake of Zn in plant systems. Adsorption mechanisms control the concentrations of zinc in the soil solution, and available zinc to plant roots. The amounts of zinc in variable forms can be desorbed and become available to plants. The exchangeable adsorption of zinc cations in soils can be expressed in this equation:



Whereas M is any other divalent cation. Zinc ions (Zn^{+2}) are held on the surface of organic matter and clay minerals. Since zinc is held on clay soil particles and by chelation, it does not move through the soil and is not leached under most conditions. (**Brian, 2008**).

2.3.7. Manganese (Mn):

Manganese is one of the 12 most abundant elements in the biosphere which makes up about 0.098% of the Earth's crust, (**Siegel et al., 2000**); (**ATSDR, 2008**). Natural levels of total manganese in soil range from < 2 to 7,000 mg/kg, with mean values of concentration averaging 330 mg/kg, (**Shacklette and Boerngen, 1984**). Manganese is considered to be one of nine primary micronutrients for plant growth. Manganese is absorbed by the plant roots in the form of Mn^{2+} . Manganese plays an important role in photosynthesis, production of proteins and amino acids, the synthesis of

various enzymes, chlorophyll formation, nitrogen metabolism and nitrate reduction (**Eun et al., 2010**).

Manganese deficiency symptoms in the plants are: young leaves, interveinal chlorotic mottling of immature leaves, the veins themselves remain dark green, but yellowing color between the veins of the leaves and flower buds often do not fully develop, turning yellow. In severe deficiency, yellow color shows clearly, necrotic spots usually appear in the interveinal tissue. The deficiency of manganese in soil is treated with manganese fertilizers in specific amounts. Manganese is an essential nutrient for all crops, but it can also be toxic when present in excess. Several symptoms which develop in plants as a result of increase in manganese include: darkening of leaf veins, usually on older foliage, and necrotic blotching of foliage (**Eun et al., 2010**).

Manganese present in soil originates from both natural and anthropogenic sources, atmospheric deposition and mineral weathering. Manganese exists in more than one oxidation state in the soil: namely Mn^{2+} , Mn^{3+} and Mn^{4+} . (**Henry and Boyd, 1988**); (**Eun et al., 2010**); (**McBRIDE and M.B, 1994**).

There are several soil conditions that influence manganese availability to plants, which include: pH, organic matter, moisture, and temperature.

1. pH: at high pH, manganese forms bonds with organic matter, decreasing its solubility. So manganese can precipitate as MnO_2 and is removed from the solution, leading to lower manganese,

decreasing manganese availability. **(Eun et al., 2010); (Henry and Boyd, 1988); (KABATA et al., 2001); (McBRIDE, 1994).**

2. Organic matter: at high pH, organic matter soils are more likely to show manganese deficiencies because Mn^{+2} is readily chelated by organic molecules, which makes the manganese less available at pH above 6.5. Therefore, soils high in organic matter result in manganese deficiency. **(Eun et al., 2010); (Schulte and Kelling, 1914).**

2.4. Fertilizers:

One of the important factors in the world that play a vital role and are widely used in agriculture is fertilizers. Fertilizers are an important element in the food production, they offset nutrient deficiency in soil, they also increase the crop yields by maintaining soil fertility. Since the early 1900s, the use of fertilizers started. As the population grows, more agricultural output will be required, so more and more fertilizers are applied, in the following years, especially in developing countries, to increase the crop productivity in the soil that suffer from nutrient deficiency. **(Clark and Kelly, 2004).**

In Palestine, because of the tightness of agriculture areas and the large increase in population, people have to use fertilizers to increase the yield of agriculture land. In the west bank two kinds of fertilizers are used, organic fertilizers (animal manure) and inorganic (chemical) fertilizers. Annually, 30,000 tons of chemical fertilizers and manures are used in agricultural

areas, (PCBS, 2012); (Applied Research Institute – Jerusalem). For instance, in the growing season of 1995-1996, the total annual quantity of chemical fertilizers applied was estimated about 18,980 tons. Nablus city is located on agriculture lands, so that farmers in it use chemical fertilizers extensively without planning to supply the plants with nutrients which helps the plants grow. Some examples of chemical fertilizers and quantities used in west bank and in Nablus city are shown in table (2.2).

Table (2.2): Average types and quantities of chemical fertilizers applied to irrigated crops in the west bank.(Applied Research Institute- Jerusalem).

Types of fertilizer	Quantity (Kg/ha)		
	Vegetable crops	Fruit trees	Field crops and forages
Super phosphate	750	500	500
Compound fertilizers (N, P, K)	500	500	300
Ammonium sulfate	800	300	200
Urea	250	200	-
Micro-nutrients	15	30	-
Total	2315	1530	1000

Fertilizers and the fertility of soil play a major role in world food production to the overall economic activity in countries, (Henry and Boyd, 1988). Inorganic fertilizer has now been subsidized in developing countries for five decades. It consists of adding chemical fertilizers to the soil. (Johannes,2013); (Clark and Kelly, 2004). In Asia, the use of inorganic fertilizers has increased because its contribution increased the production of crops. It also increased the production of biomass, cut down on soil erosion, and enriched the supply of humus to the soil. (Johannes, 2013).

The intensive use of chemical fertilizers supplied the soil with metals to replace those withdrawn by the crops, **(Wolman and Fournier, 1987)**.

Having the plants to grow well and to complete the life cycle requires several nutrients. The main nutrients which are macronutrients are phosphorus (P), nitrogen (N), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), and essential micronutrients, **(Johannes, 2013); (Raymand and Felix,2011)**. Different nutrient compositions suit soil types and different crops. Inorganic fertilizers are commercially manufactured, and they contain a vast array of nutrient compositions and concentrations which enrich soil fertility, and help the plants grow. Some fertilizers contain one main nutrient source, while others contain multiple sources. **(Clark and Kelly, 2004); (Johannes, 2013)**. Therefore, chemical fertilizers allowed the farmers to cultivate the same field with the same crop, season after season, without losses in the fertility of the soil, because they permitted the intensification of land use by speeding crop rotation. **(Clark and Kelly, 2004); (Wolman and Fournier, 1987)**.

Some soils lack the heavy metals as (K, N, P, Cu, Mn, Mo, Fe, Zn, and Ni) that are important for healthy plant growth, **(Raymand and Felix, 2011)**. Commercial compound fertilizers are commonly added to the soil to supply the crops with these metals. Large quantities of fertilizers (compound fertilizers) in a mixture of potassium (K), nitrogen (N) and phosphorus (P) are regularly added to soils in intensive farming systems to provide adequate amount of these metals for crop growth. The compound fertilizers also contain trace amounts of heavy metals (e.g., zinc (Zn), iron (Fe),

copper (Cu), cadmium (Cd) and lead (Pb)) as impurities to meet the nutrient needs of the desired crop, **(Raymand and Felix, 2011); (Andrew et al., 1914)**. However, application of certain fertilizers in inappropriate quantities leads to potentially toxic effects to the soil. **(Raymand and Felix, 2011); (Andrew et al., 1914)**.

The percent of potassium, nitrogen and phosphorus in compound fertilizers are different. For example, a 15/30/15 compound fertilizer contain 15% total nitrogen, 30% phosphorus, and 5% soluble potassium, the remaining 40% could be any combination of secondary macronutrients, micronutrients, and inactive ingredients. The same ratio of primary ingredients are found in a 5/10/5 fertilizer, but the concentrations are three times as low, therefore, the 5/10/5 fertilizer is less nutritious per unit weight than the 15/ 30/ 15 fertilizer. **(Clark and Kelly, 2004)**.

Chemical Fertilizers are necessary to maintain global crop productivity at specified levels, and it will be more important if yields are to be increased. But inadequate and unbalanced use of chemical fertilizers in many developing countries as Asian countries, leads to negative impacts on crop quality. Because of the excessive use of fertilizers, heavy metals increase in the soil above allowable limits. This led to the negative impact of fertilizers on the soil, environments, climate, human health and safety, **(IFA Statistics, 2007); (Tomoyuki et al., 2010); (Johannes, 2013); (International Fertilizer Development Center, 2001)**. Examples include nitrate pollution in surface and ground water, **(Clark and Kelly, 2004)** and more chemical residues accumulate over time in the soil, **(Wolman and**

Fournier, 1987). For example, in Palestine the groundwater will be enriched with chemical fertilizers as nitrate, because the rains and irrigation in winter wash remnants of chemical fertilizers into it. After several years this has become a matter of concern (**Wolman and Fournier, 1987**). So, historically, fertilizers that are used in agriculture were the first major human influence on the soil. Generally, the most important issues facing soil in Palestine is the extensive use of fertilizers (**PCBS, 2012**).

2.5. Previous study:

Background knowledge of the sources and the accumulation of heavy metals in soils is important for the selection of appropriate remedial options to enhance food security. Several studies found that heavy metals pollute the soil from several sources like fertilizers. (**Raymond and Felix, 2011**).

In Japan, it was found that fertilizers used in a sample of red soil that differ in pH contained heavy metals such as cadmium, copper and zinc. Results indicate that the concentration of Cd is within the allowable concentration in Japan, but the concentrations of Cu and Zn are more than the allowable concentration under Japanese regulations. These two heavy metals and others cause soil pollution. Table (2.3) shows the target metals and concentration standards for pollution of soils in China. (**Tomoyuki et al., 2010**).

Table (2.3): Target metals and concentration standards (ppm oven-dry soil), for pollution of soils in China (Ministry of Environmental Protection, 1995).

Metal	pH less than 6.5	PH 6.5-7.5	pH more than 7.5	pH more than 6.5
Cd	0.3	0.3	0.6	1
Cu	150	200	200	400
Zn	200	250	300	500

Fertilizers which were put on 20 samples of sandy loam soil in different areas with pH (9-9.2) in Baquba city (north east of Baghdad) resulted in soil contamination with heavy metals as Zn, Ni, Cr and Pb at levels above the allowable concentration in the international soils, while the concentrations of Co, Fe and Co were under the allowable concentration in the international soils. For instance, the concentration of iron in the samples was about (15304ppm- 29885 ppm) and the concentration of zinc in the same samples was about (80 ppm- 156 ppm). (**Kareem et al., 2010**).

When using fertilizers in several samples of sand soil at certain depths in Nigeria, results showed that the soil samples contain heavy metals as Cu, Cd, Zn, Mn and Pb. The results also showed that the total metal concentration after long term use of fertilizer was in the following order Mn>Zn>Pb>Cu>Cd. The concentration of the heavy metals in fertilized soils was more than unfertilized soil. Table (2.4) shows the results for total metal concentrations in the soil samples investigated. (**Ajayi1 et al., 2012**).

Table (2.4): Total metal concentrations in soil samples (Ajayi1 et al., 2012).

Sample	Depth (cm)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Cd (ppm)	Pb (ppm)
CUT	0 – 15	348	51.6	4.59	0.82	8.69
CUS	15 -30	317	56.4	2.52	0.82	<4.34
CFT	0 – 15	498	78.1	9.0	<0.23	11.9
CFS	15 -30	522	91.1	13.0	1.05	6.52
VUT	0 – 15	1597	166	11.0	1.14	63.0
VUS	15 -30	1518	130	19.4	0.87	48.3
VFT	0 – 15	1897	165	17.2	1.87	64.6
VFS	15 -30	1678	131	17.8	1.1	46.7
PT	0 – 15	306	44.2	5.91	0.54	27.1
PS	15 -30	231	21.6	6.77	<0.23	9.78
FT	0 – 15	869	107	12.9	0.46	50.0
FS	15 -30	652	64.8	9.98	0.78	15.7

The heavy metals such as Mn, Zn, Cu, Cr, Cd, Ni and Pb in different samples of red soil at different depths in Iraq showed results indicate that the concentration of the most heavy metals is increased in the surface layers of soil at 0-20 depth, compared to the other depths, which indicates the presence of kinetics and transmission of these metals through the layers of the soil. Table (2.5) shows the concentration of some heavy metals in several samples of soil. Figure (2.7) showed the contrast of the concentration of some heavy metals in the study soil. (Ghufran, 2010).

Table (2.5): The concentration of some heavy metals in several samples of soil (ppm). (Ghufran, 2010).

Cd	Mn	Ni	Pb	Zn	Cu	Cr	العمق سم	التربة
0.159	395	121.2	18	65.2	12	50	20 -0	تربة الكرفس
0.09	390	112	19	61.2	9	50	50 -20	
0.1	392.5	116.6	18.5	63.2	10.5	50	المعدل	
0.11	349	116	11.1	38.4	10	22.5	20 -0	تربة الفجل
0.065	356.4	116	9.4	41.2	10	27.5	50 -20	
0.1	352.7	116	10.2	39.8	10	25	المعدل	
0.036	289.5	109.8	7.5	45	9.5	51.7	20 -0	تربة الشعير
0.025	290	107.9	7.35	45.4	8.5	46.3	50 -20	
0.03	285	108.8	7.4	45.2	9	49	المعدل	
0.077	349.8	100.5	6.9	54	8.5	39.2	20 -0	تربة البرسيم
0.11	350.2	97.3	4.3	46.2	6.3	39	50 -20	
0.09	350	98.9	5.6	50.1	7.4	39.1	المعدل	
0.08	345.02	110.1	10.42	49.575	9.225	40.775	معدل التراكيز	
3	2000	50	100	300	100	100	محددات WHO	

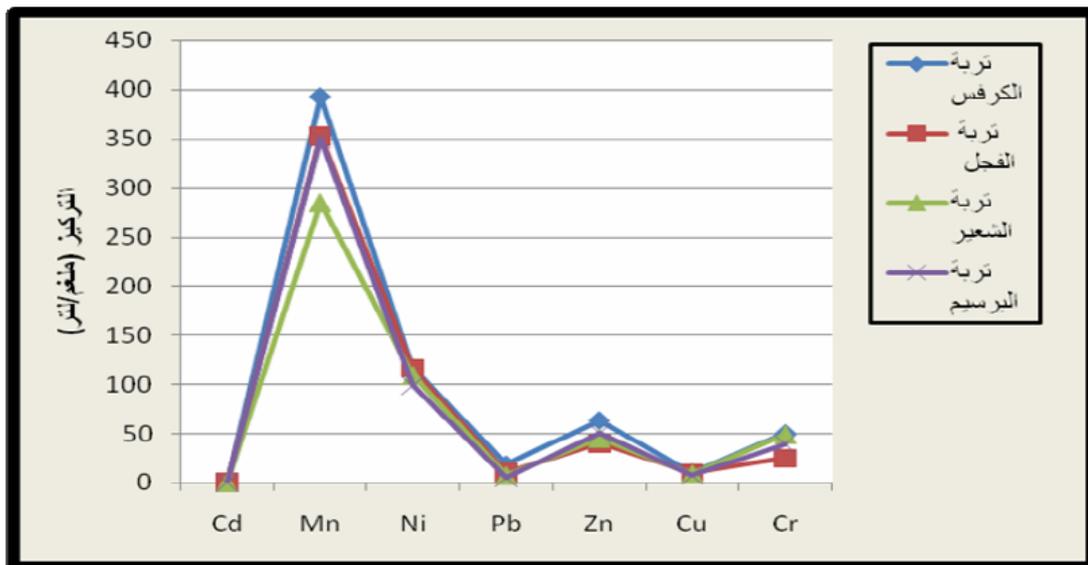


Figure (2.5): The contrast of the concentration of some heavy metals in the study soil (Ghufran, 2010).

Kinetic studies (Freundlich adsorption isotherm) were applied in three sandy loam soil samples in Talkarm. The samples had different concentrations of nitrate, which leached from the soil, and the adsorption of the nitrate ion was studied. The results of the adsorption study of the three samples were found to be 0.611, 0.779 and 0.821 respectively, while the concentration of nitrate ions was 263.3 mg/L, 216.7 mg/L and 799 mg/L respectively. **(Osama et al., 2011).**

Nitrogen and phosphate fertilizers that were used in Egypt, in addition to potassium fertilizers, which were imported from abroad, were put on loam and sand soil. It was found that these fertilizers contained varying amounts of heavy metals such as Ni, Cd and Pb. The phosphate fertilizers contain a large amount of heavy metals, where as Nitrogen fertilizers contain less quantity. **(Ahmad, 2008).**

Langmuir equation was used in different areas of adsorption of cadmium in the soil in the Al-Hassa area (sand and clay sand). Results showed a relationship that describes the adsorption of cadmium in this soil, 625micrograms/g soil and 2000micrograms/g soil. The increased concentration of cadmium in the least active sites allows cadmium adsorption in the same way as equivalent to the Langmuir equation. **(Mohammad et al., 2010).**

The heavy metals such as Zn, Cu, and Pb in different samples of clay loam soil at different depths in Salim and Deir Sharaf in the city of Nablus, results indicate that the concentration of these heavy metals increasing in the soil and leachate due to irrigating the soil with water polluted with these heavy metals. **(Inaya et al., 2000).**

2.6. Summary:

Soil heavy metals contamination has been the focus of many studies first Tomoyuki Makino study the soil Contamination of heavy metal (Cd, Cu and Zn) in red soil samples in Japan at different pH of soil, (pH less than 6.5, pH 6.5-7.5, and pH more than 7.5) (Tomoyuki et al., 2010). Second Kareem Khwedim studied the concentration of heavy metals (Zn, Ni, Cr and Pb) in twenty samples of sandy soil, that are polluted with fertilizers in different areas in Baquba city in Baghdad. This study analyzed the effect of more than one factor on this process such as Iron oxides, Clay minerals, Organic factors and pH (Kareem et al., 2010). Third S.O. Ajayi studied the concentration of heavy metals (Cu, Cd, Zn, Mn and pb) in several samples of sand soil in Nigeria that are pollute with fertilizers, at different depth (0-15 cm and 15-30 cm), pH and organic matter in the soil were calculated (Ajayi1 et al., 2012). Fourth Ghufran Farouq study the concentration of heavy metals (Mn, Cu, Zn, Cr, Cd, Ni and Pb) in different agricultural red soil, plants and water near the agricultural soil in Iraq, at different depth (0-20 and 20-50) samples of soil was examined (Ghufran, 2010). Fifth Osama Zaki study the kinetics of Ground water Nitrate (NO_3^-) in three sandy soil loam that leachate in Tulkarem city in Palestine, by using soil columns at different depth, Freundlich adsorption isotherm were applied on the study (Osama et al., 2011). Sixth Ahmad Aziz study the concentration of heavy metals (Ni, Cd and Pb) in several samples of loam and sand soil in Egypt, that pollute with Nitrogen and phosphate fertilizers at different depth (0-30 cm, 30-60 cm) (Ahmad, 2008). Seventh

Mohammad Abd Al-Rahman Study the concentration of heavy metal (Cd) in several samples of sand and clay sand soil, that pollute with phosphate fertilizer in Alhasa area in Saudi Arabia at different depth (0-30 and 30-60), leachate water and also the concentration of Cd in cultivated plants in the previous soil was measured, Langmuir equation was applied in this study (Mohammad et al., 2010). Eightieth Inaya Mized study the concentration of heavy metals (Zn, Cu and Pb) in different samples of caly loam at different depth in salim and deir Sharaf in Nablus city in Palestine by using soil columns (Inaya et al., 2000).

In our study the concentration of heavy metals (Zn, Mn, Cu and Fe) and nutrients (K_2O , P_2O_5 and NO_3^{-1}), in several samples of red soil that are polluted with compound fertilizer in different depth (0 cm, 54 cm, 90 cm and 135 cm), in east Nablus Palestine were measured, also the concentration of heavy metals and nutrients in water leached from the previous soil samples were measured, this study was conducted by using soil columns. It is an important study in Palestine specially in east Nablus were it is an agricultural area and compound fertilizer used in Nablus in large quantities. Long term use of compound fertilizer for agricultural purposes, leads to accumulation of toxic heavy metals in the soil that damage plants, and animals and human and environment.

Chapter Three

Methodology

3. Methodology:

3.1. Experimental Set up:

Experiments were conducted in the laboratory at An-Najah National University. The experimental part of this research focuses on studying kinetics and the evaluation of heavy metals and nutrients in leachates from fertilizers in Nablus. The red soil was collected from the east Nablus district. Also, the fertilizer was purchased from Nablus. Several analyses of nutrients (phosphate, nitrate, and potassium), heavy metals (zinc, copper, manganese, and iron) were conducted on the leachate water samples and fertilized soil samples. Physical and chemical characteristics of red soil such as soil texture, water content, specific gravity, pH of soil, and organic carbon were measured to evaluate pollutant (heavy metals and nutrients) accumulation and leaching to the ground water, resulting from application of fertilizer that contain heavy metals on soil. Statistical analysis was conducted using IBM SPSS v24.0. Linear Regression test.

3.2. Experimental program:

3.2.1. Samples collection:

The red soil was obtained from the east Nablus district, and the fertilizer 20/20/20 was purchased from Nablus in Palestine. Red soil and compound fertilizer were both analyzed without further treatment.

3.2.2. Soil Column Preparation:

In this study, two soil PVC plastic columns were prepared measuring 1.5 meter long and six inch diameter. At the end of each column a funnel was installed and a sieve was put inside of it. A tap of water was connected at the end of the funnel, and a bottle was placed under each tube to collect liquid samples, as shown in the following figure, (3.1) and (3.2).



Figure (3.1): Soil column apparatus

The sample of red soil was collected from east Nablus district. Red soil was sieved, and filled inside the columns and was rinsed with distilled water. Fertilizer solution was added to the soil in the first columns, the second column was used as a blank control using distilled water.

A 100 gram of compound fertilizer was dissolved in two liters of distilled water. The mixture was added to the first column on the first day, and the water leachate was collected in the next day. The same process was conducted every five days during one month. Five samples of water leachate were collected as shown in the figure, (3.1.b).

For the control, two liters of distilled water were added to the second column in the first day, and the water leachate was collected in the next day, the same process was conducted every five days during one month. Five samples of water leachate were collected.



Figure (3.2): Soil column apparatus

Then every column was cut into four sections, at heights of 0 cm, 45 cm, 90 cm and 135 cm. as shown in the figure, (3.3).

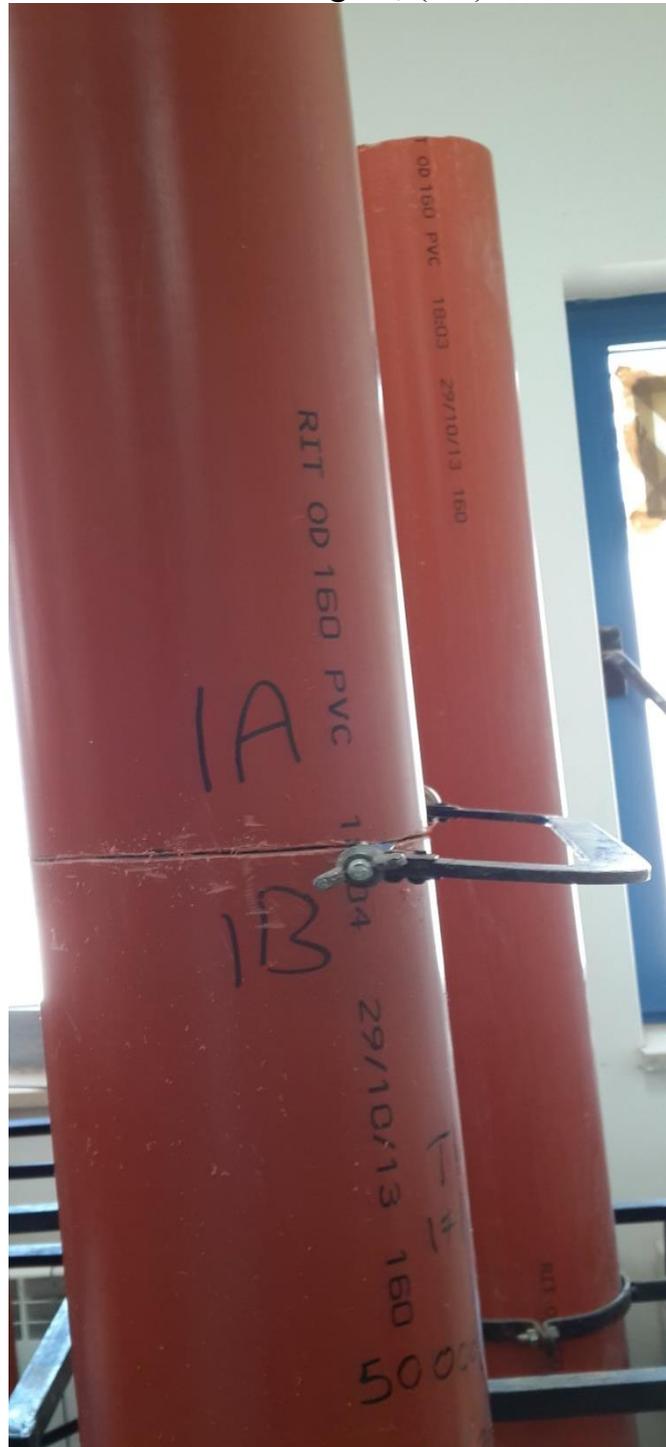


Figure (3.3): cutting Soil column

All samples of water, fertilizer and soil were analyzed to measure the concentration of each of the following metal ions: Zn^{+2} , Mn^{+2} , Cu^{+2} , Fe^{+3} , NO_3^- , K_2O and P_2O_5 . The number of all samples that were analyzed was twenty. After these steps eight samples of soil were collected.

3.2.3. Instrumentation:

Flame atomic absorption (FAA), Spectrometer model icE – 3000 SERIES, Serial number C113500021, UK. was used for the analysis of Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3} .

Ultraviolet visible (UV-VIS SHIMADZU), Model No: UV - 1601 method was used for the analysis of potassium (K) as K_2O , phosphorus (P) as P_2O_5 , and nitrogen (N) as NO_3^- in several samples of red soil, fertilizers and leachate, using the 234nm wave length for potassium, 880 nm wave length for phosphorus, and 410 nm wave length for nitrogen as nitrate. Photometer nitrate instrument was used to determine the concentration of nitrogen as nitrate in several samples of water leachate.

Hydrometer type (ASTM 152 H), for analysis of soil.

JENWAY (3510) pH Meter was used to measure pH.

3.2.4. Chemicals and Reagents:

Chemicals and reagents used in this study:

- Compound fertilizers: 20/ 20/ 20 (N, K, P) from Nablus.
- Copper(I) Nitrate (CuNO_3), Nitrate reagent and Sodium metasilicate anhydrous Na_2SiO_3 from Sigma-Aldrich.
- Diphenylamine indicator from Fluka.
- Ferrous ammonium sulfate, hydrazin hydrate and manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) from Riedel-deltaen.
- Perchloric acid (HClO_4) from Merck.
- Phenolphthalein from ICN Biochemical.
- Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) from Carloerba.
- Potassium dihydrogenphosphate (KH_2PO_4) and ammonium molybdate from Sigma.
- Potassium nitrate (KNO_3) and potassium chloride (KCl) from Frutarom.
- Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), iron(III) chloride (FeCl_3) and salicylic acid from Alfa Aesar.

3.3. Sample Digestion:

3.3.1. Digestion of fertilizer:

5 g of fertilizer was dissolved in 20 ml of conc. nitric acid (HNO_3) to 200°C , until the fertilizer dissolved; the solution was cooled, placed in a flask, and distilled water was added to have a final volume of 50ml.

(Mohammad, et al. 2010).

3.3.2. Digestion of soil:

The soil was dried and sieved with 2mm sifts. 0.25 of soil was weighed in Erlenmeyer flask. 4 ml of nitric acid (HNO₃) was added; then 1ml of perchloric acid (HClO₄) was added. The solution was heated to 105 °C for 2-3 hours until the white fumes appeared. The temperature was raised to 185 °C, until the solution was dried. The remaining substance was cooled. 2ml of 5M of hydrochloric acid (HCl) was added. The solution was heated to 60 °C for 1 hour. After it was cooled, 8ml of distilled water were added and it was left for 4 hours. The solution had a final volume of 50 ml with distilled water. (Ghufran and Ryad, 2010).

3.4. Laboratory analysis:

3.4.1. Soil Analysis:

One kilogram of soil was sieved by a 2 mm sieve, and then dried at 105 °C. Several tests on the soil were done before any treatment, as the following:

3.4.1.1. Soil Texture (Hydrometer Test):

Hydrometer analysis is a widely used method for the determination of size distribution of soil particles, by the No. 200 (0.075 mm) sieve to 0.001 mm. The hydrometer analysis is based on Stokes Law. that shows the relationship between the velocity of fall of spheres in a fluid, the specific weights of the sphere, the diameter of the sphere, and the fluid viscosity.

The equation from the previous relationship is:

$$V = (V_s - V_w D^2) / 18 \eta$$

Where:

V: velocity of fall of the spheres (cm/s).

η : viscosity of the fluid (g.s / cm²).

D: diameter of the sphere (cm).

V_s: unit wt. of soil solids (g / cm³).

V_w: unit wt. of water (g / cm³).

$$V = L / t$$

The final diameter of soil particles is given by the following equation:

$$D = A\sqrt{L(cm)/t(min)} .$$

Procedure: The soil texture was determined by ASTM H-152 hydrometer device, before this step, 40g of soil was sieved using 2mm sieve, and dried at 105°c for 24 hours by Elle oven.

3.4.1.2. Moisture (Water content):

To know the relationship between the way in which soil behaves and its characteristics, it is important to know the water content of the soil. Water content is defined as the ratio of the weight of water in a given soil mass, to the weight of solid particle.

Procedure: The mass of the dry empty crucible (W₁), the closed crucible with the moist soil (W₂) were recorded. The crucible with soil was put into the oven for 24 hours at 110° C. The mass of the closed crucible with the dry soil was recorded (W₃). (**Isam and Ahmad, 2010**).

The moisture content for the soil (W) was determined using the following equation:

$$w(\%) = \frac{W_2 - W_3}{W_3 - W_1} \times 100$$

Where:

($W_2 - W_3$): the weight of moisture.

($W_3 - W_1$): the weight of dry soil.

3.4.1.3. Specific Gravity:

Specific gravity (G_s) is defined as the ratio of the weight of a given volume of substance to the weight of an equal volume of distilled water at 4°C.

Procedure: Volumetric flask (100 ml) was filled with distilled water to the mark. The weight of the volumetric flask with water was recorded (W_1). 20g of dry soil was weighed. Distilled water was added until flask was about two-thirds full. The flask was attached to the vacuum for 15-20 minutes. Distilled water was added carefully to the 100 ml mark. The weight of the flask, soil and water was recorded (W_2). The flask was emptied into an evaporating dish. The dish was placed in the oven. The weight of the dry soil in the evaporating dish was determined (W_3).

Specific gravity is defined as:

$$G_s = P_s / P_w$$

Where:

P_s : weight of soil solids only.

P_w : weight of water at 4°C

Also specific gravity is calculated by using the following equation:

$$G_s = (W_s / V) / W_w / V$$

Where:

W_s : weight of soil solids.

W_w : weight of water.

V: volume of soil = volume of water.

3.4.1.4. pH of Soil:

To measure the pH of soil sample, 10g of air dried sample was sieved with 2 mm sieve, it was added into 100 ml distilled water, and was shook for one hour then the pH was measured.

3.4.1.5. Organic Carbon:

One gram of red soil was weighed accurately; it was put into a dry 500 ml conical flask. 20 ml of concentrated H_2SO_4 and 10 ml of 1 N of $K_2Cr_2O_7$ were added to it. The flask was heated on a hot plate, and was instantly swirled in order to mix the soil and reagent, until the temperature reached $135^\circ C$. After that, 1ml of diphenylamine indicator was added. Then 0.5 N ferrous ammonium sulfate solution was used to titrate the resulted suspension, until green color began to emerge, which indicated the end point.

By using the following equation, the carbon content was calculated.

$$\begin{aligned} \text{Organic Carbon (\%)} &= 0.003 \text{ g} \times N \times 10 \text{ ml} \times (1 - T/S) \times 100 / \text{ODW} \\ &= 3 (1 - T/S) / W \end{aligned}$$

Where:

N = Normality of $K_2Cr_2O_7$ solution.

T = Volume of $FeSO_4$ used in sample titration (ml).

S = Volume of $FeSO_4$ used in blank titration (ml).

ODW = Oven – dry sample weight (g).

% of organic matter = $1.72 \times$ % of organic carbon, (Halimah et al., 2012).

3.4.2. Determination of Heavy Metals:

Heavy metals that include Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3} were detected in this study by using Flame Atomic Absorption (FAA) Spectrometer instrument.

The stock solution of 1000 ppm was prepared for each of the following metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}).

The standard solution of 1, 5, 10, 15 and 20 ppm were prepared by dilution from the stock solutions for each of Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3} .

The fertilizer solution was prepared by dissolving 1.002 g of compound fertilizer in distilled water in 100 ml flask, equivalent to 10020 ppm. Flame Atomic Absorption (FAA) Spectrometer instrument was used to measure the concentration of the following metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}).

The same method and procedure was adopted to measure the concentration of the following metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}), in samples of water and samples of soil.

3.4.3. Determination of Nutrients:

3.4.3.1. Determination of Potassium:

3.4.3.1. a. Determination of potassium in compound fertilizer:

The determination of potassium was done by using UV spectrometer at 234 nm wave length. In this experiment three solutions were prepared:

The stock solution of KNO_3 of 1000 ppm was prepared by dissolving an accurately weighed 0.259 g of KNO_3 in distilled water.

The standard solution of 10, 25, 50, 75 and 100 ppm were prepared from the stock solution by dilution using distilled water to obtain a final volume 100ml for each solution.

The compound fertilizer solution is prepared by dissolving 0.259g of compound fertilizer in distilled water. Then 10ml of the previous solution was taken and diluted to 100 ml.

3.4.3.1. b. Determination of potassium in samples of water and soil:

The same method was used for the determination of potassium in fertilizer. However, different standard solutions were prepared: 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, 50 ppm, 75 ppm, 100 ppm, 125 ppm, 150 ppm. The final volume for each solution was 100ml by adding distilled water.

3.4.3.2. Determination of Nitrogen:

3.4.3.2.a. Determination of Nitrogen as Nitrate in ten water samples:

For the detection of nitrate by photometer nitrate instruments, the following was done:

1. The cell of the sample was taken and nitrate reagent was put in it, and then shaken vigorously for exactly one minute.
2. The cell of the sample was put in their place on the photometer.
3. After 4 minutes and 30 seconds the result of nitrate in the sample appeared on the screen of the photometer.

3.4.3.2.b. Determination of Nitrogen as Nitrate in one compound fertilizer sample:

A 0.5027 g of fertilizer was weighed. It was soluble in distilled water then diluted to the mark in 100ml volumetric flask.

A 10ml of fertilizer sample solution was taken and the same procedure as water sample was followed to measure the nitrate in the fertilizer sample.

3.4.3.2.c. Determination of Nitrogen as Nitrate in the ninth sample of red soil:

For the detection of nitrate by UV spectrophotometer at 410 nm wavelength, we performed the following procedure:

Procedure:

1. 2M of potassium chloride stock solution (KCl) was prepared by dissolving 37.5 g of KCl in 250ml of distilled water then the volume was diluted to the mark.
2. 5g of every sample of red soil was weighed, and then 25ml of 2M KCl was added.
3. Extraction vessels were placed on reciprocating mechanical shaker.
4. The process of shacking continued for thirty minutes.
5. The filter was extracted and taken to continue the procedure.
6. 0.25ml of extract was taken into 50ml Erlenmyer flask.
7. 0.8ml of 5% salicylic acid in conc. H_2SO_4 was added.
8. 19ml of 2N of NaOH was added after 20 minutes at room temperature.

9. Samples were cooled to room temperature.
10. Five calibration standard solutions were prepared: 10 ppm, 40 ppm, 60 ppm, 100 ppm and 200 ppm. The same previous procedure was followed.
11. The absorbance of nitrate was measured at 410 nm by UV-Spectrophotometer.

3.4.3.3. Determination of Phosphorus:

For the detection of phosphorus by ultraviolet visible spectrophotometer at 840 nm wavelength, we prepared four solutions:

1. Phosphate stock solution was prepared by dissolving 0.717g of potassium dihydrogenphosphate KH_2PO_4 in distilled water in 500ml volumetric flask to form concentration 1434 ppm.
2. Ammonium molybdate (2.5%) was prepared by diluting 50 ml of 5% ammonium molybdate reagent in 100 ml of volumetric flask.
3. Sulphuric acid solution (10 N) was prepared by diluted 28ml of conc. Sulfuric acid in 100ml of volumetric flask.
4. Hydrazine hydrate (0.5 M) was prepared by taking 2.44ml of conc. hydrazine hydrate and diluted in 100ml volumetric flask.

Water sample preparation: samples of water were filtered by filter paper to remove the insoluble particles. Then a few drops of 2N of H_2SO_4 were added, followed by heating for about 30 minutes.

Soil sample preparation: after the digestion of the soil, the solutions were taken and the same procedure for water samples was done.

Fertilizer sample preparation: 5 gram of compound fertilizer was weighed, which was then dissolved in 100ml distilled water. The sample was filtered by filter paper; the filtrate was put in 100ml volumetric flask. Standards solution curves were prepared from stock solution: 5, 10, 15, 25, 50, 75, 100, 125, 150, 175 and 200 ppm.

Procedure for determination of phosphate in all samples:

1. 1ml of sample was taken and put in 25ml volumetric flask, 2ml of 2.5 % of ammonium molybdate and 0.5ml of 10 N sulphuric acid solutions were added. Then the solution was shaken well.
2. Distilled water was added to increase the volume to the mark.
3. The solution was left at least for about 45 minutes for maximum color development.
4. Phosphate was measured at 840 nm.
5. From the calibration curve the amount of phosphate was obtained.

Chapter Four

Results and Discussion

Results and Discussion:

The results of this work are represented in tabular and graphical form. The results show the concentration of some heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}), and some nutrients (K_2O , NO_3^- and P_2O_5) in red soil and compound fertilizer.

4.1. Soil Tests:

A sample of red soil was analyzed in order to evaluate the soil texture (hydrometer test), moisture, specific gravity, and pH value. Table 4.1 shows the results obtained from these tests.

Table (4.1): Specific gravity, moisture, texture, and pH for soil before fertilization.

Soil Properties	Results
Specific Gravity	2.72 g/cm ³
Moisture content	8.3 %
pH value	8.73 – 8.75
Organic Carbon %	5.2 %
Organic Matter %	8.944 %
Soil texture	Clay

From the previous table it was noticed that the percent of organic carbon and organic matter was large, which indicates that high percentage of adsorption occurs for the heavy metals ions (Zn^{+2} , Mn^{+2} , Fe^{+3} and Cu^{+2}) and macronutrients (K_2O) due to the positive charge of the previous heavy metals, macronutrients K^{+1} and negative charge of clay soil, while low percentage of adsorption will occur for the macronutrients (NO_3^- and P_2O_5) due to the negative charge of the previous macronutrients, that prevents the link with the negative charge of clay soil. It was noted that the pH of red

soil is basic, which indicates that a high percentage of adsorption on the surface of the soil will occur for the heavy metals ions (Zn^{+2} , Mn^{+2} , Fe^{+3} and Cu^{+2}).

4.2. Determination of the concentration of some Heavy Metals:

The concentration of four heavy metals ions (Zn^{+2} , Mn^{+2} , Fe^{+3} and Cu^{+2}) was determined in nine samples of soil (one before fertilizer and eight after fertilizer), ten samples of water which leachate from the soil fertilization, and one sample of compound fertilizer. The results are represented in Table (4.2).

Table (4.2): Heavy metals ions concentration in the nine samples of soil, ten samples of water which leachate from the soil fertilization, and one sample of compound fertilizer.

Name of Sample	(Fe⁺³) con. Ppm	(Cu⁺²) con. ppm	(Mn⁺²) con. ppm	(Zn⁺²) con. Ppm
11 (water leachate)	0.3829	0.0099	0.589	0.4083
12 (water leachate)	1.6956	0.0123	1.691	1.9846
13 (water leachate)	3.4700	0.0166	2.8786	4.6706
14 (water leachate)	.59447	0.0248	4.6743	6.9104
15 (water leachate)	7.3545	0.0279	5.98	9.1713
Mean	3.8	0.02	3.2	4.6
21 (blank) (water leachate)	0.0310	0.00067	0.0035	0.0421
22 (blank) (water leachate)	0.0383	0.0098	0.0091	0.0567
23 (blank) (water leachate)	0.0515	0.0126	0.0113	0.0712
24 (blank) (water leachate)	0.0530	0.0134	0.0135	0.0911
25 (blank) (water leachate)	0.1974	0.01640	0.0292	0.2101
Mean	0.07	0.01	0.01	0.09
WHO Standards	0.5	1	0.5	5
1A0 (soil)	1220.5988	125.7741	418.7278	370.7326
1AB45 (soil)	753.2593	75.5294	254.8914	235.9053
1BC90 (soil)	519.9217	50.4057	171.5628	175.6273
1C135 (soil)	284.1224	25.2801	87.155	50.6396
Mean	694.5	69.2	233.1	208.2
2A0 (blank) (soil)	48.3621	0.16122	2.6141	0.5412
2AB45 (blank) (soil)	48.323	0.15142	2.605	0.4350
2 BC90 (blank) (soil)	48.2723	0.13882	2.4920	0.4132
2 C135 (blank) (soil)	48.0211	0.10921	2.4492	0.1123
Mean	48.2	0.14	2.5	0.38
WHO Standards	38000	2 – 100	2000	10 – 300
The red soil before fertilizer	48.3933	0.1620	2.6178	0.5839
Compound fertilizer sample	236.112	25.128	84.618	40.464

It is noted from table (4.2) that there is an increase in the concentration of all heavy metals (Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2}) in fertilized water samples, compared with the blank samples, this is due to the use of fertilizers which contain heavy metals. Due to the high concentration of these heavy metals ions in fertilizer, they dissolve in water and leachate in the lower layers of the soil until they reach the ground water and pollute it. The results showed that when the concentrations of all heavy metals (Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2}) increase, there is an increase of it in the leachate water samples, $\text{Zn}^{+2} > \text{Fe}^{+3} > \text{Mn}^{+2} > \text{Cu}^{+2}$, with mean 46 ppm Zn^{+2} , 3.8 ppm Fe^{+3} , 3.2 ppm Mn^{+2} , and 0.02 ppm Cu^{+2} .

It has been observed that the concentration of zinc, iron and manganese ions in water samples were found to be higher than the world health organization (WHO) acceptable maximum which is 5mg/L of Zn^{+2} , 0.5mg/L of Fe^{+3} , and 0.5 mg/L of Mn^{+2} . However, the copper concentrations in water samples were lower than the World Health Organization (WHO), where the acceptable maximum is 2mg/L of Cu^{+2} . This means that heavy metals such as Zn^{+2} , Fe^{+3} and Mn^{+2} cause pollution of the ground water, but Cu^{+2} does not pollute the ground water.

Also it is noted from table (4.2) that there is an increase in the concentration of all heavy metals (Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2}) in samples of fertilized soil, compared with the blank samples. This is due to the use of fertilizers which contain heavy metals with a positive charge that link with the negative charge of clay soil. The results showed that with time there is a decrease in the concentrations of all heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and

Fe^{+3}) in the bottom layer of fertilizer soil samples, $\text{Fe}^{+3} > \text{Mn}^{+2} > \text{Zn}^{+2} > \text{Cu}^{+2}$, with mean 694.5 ppm Fe^{+3} , 233.1 ppm Mn^{+2} , 208.2 ppm Zn^{+2} , and 69.2 ppm Cu^{+2} . This means that Fe^{+3} is the heavy metal which accumulates the most in the soil than the other heavy metals. This was followed by Mn^{+2} , Zn^{+2} , and Cu^{+2} . The accumulation of Cu^{+2} in the soil is not dangerous to the environment due to the stability of its compound in the soil, but the accumulation of Zn^{+2} in the soil was toxic.

It has been observed that the concentration of both iron and manganese in fertilized soil agrees with the World Health Organization (WHO), where the acceptable maximum of the previous metals is the following: 2000 ppm of Mn^{+2} and 38000 ppm of Fe^{+3} , while copper and zinc ion concentrations were found to be higher than the World Health Organization (WHO), where the acceptable maximum is 100 ppm of Cu^{+2} , and 300 ppm of Zn^{+2} . This means that the heavy metal Zn^{+2} caused pollution to the environment, while Cu^{+2} did not, due to the formation of a stable compound.

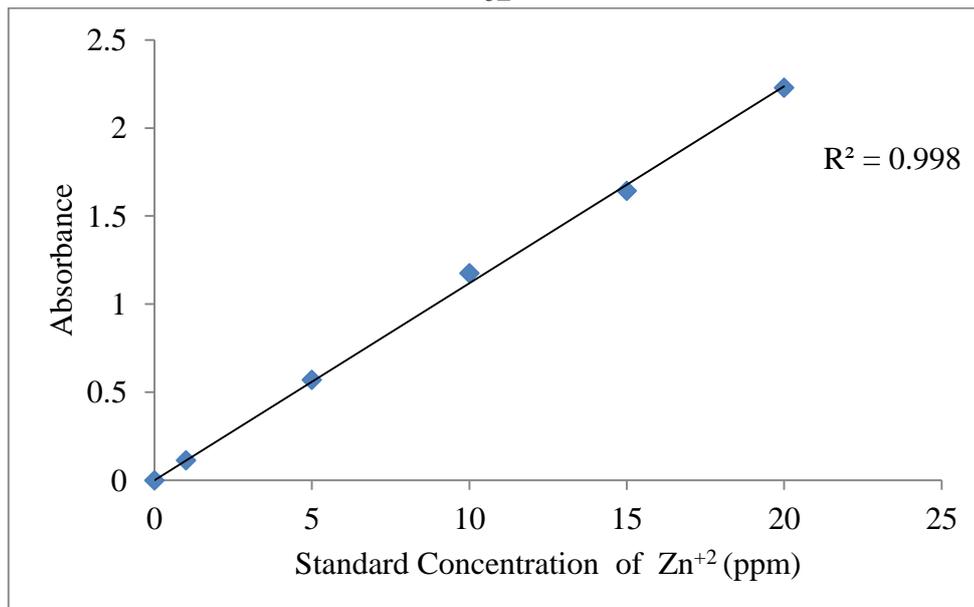


Figure (4.1.a): Calibration curve of zinc (Zn²⁺)

Stock solution of 1000 ppm of ZnSO₄.7H₂O was used to prepare different concentrations 1, 5, 10, 15 and 20 ppm, The samples were then scanned by Flame Atomic Absorption Spectrophotometer. A calibration curve was produced by plotting the absorbance versus Zn²⁺ concentration. The curve is shown in figure 4.1.a. A linear relationship was obtained over the studied concentration range.

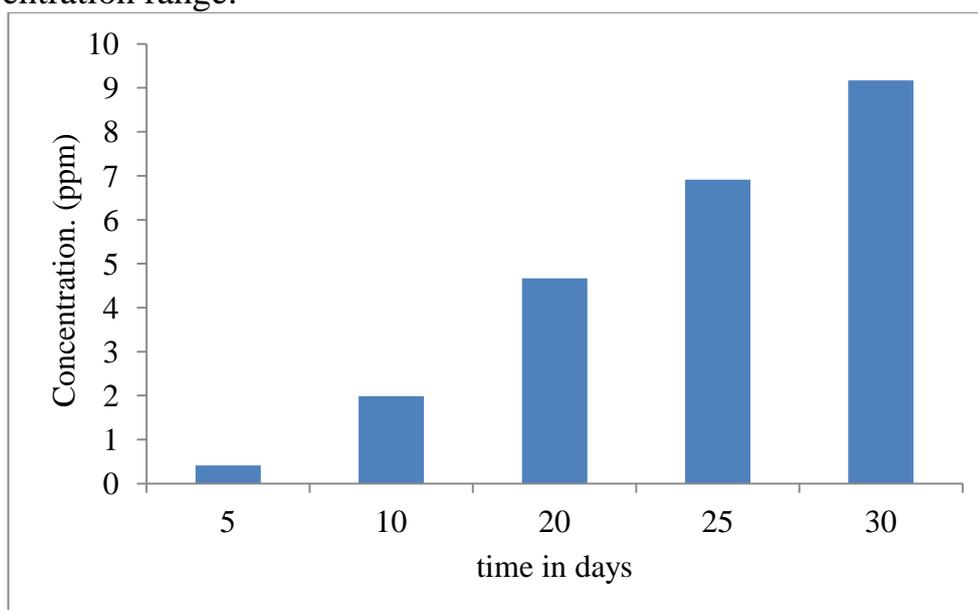


Figure (4.1.b): Plot of concentrations of zinc (Zn²⁺) in leachate water samples.

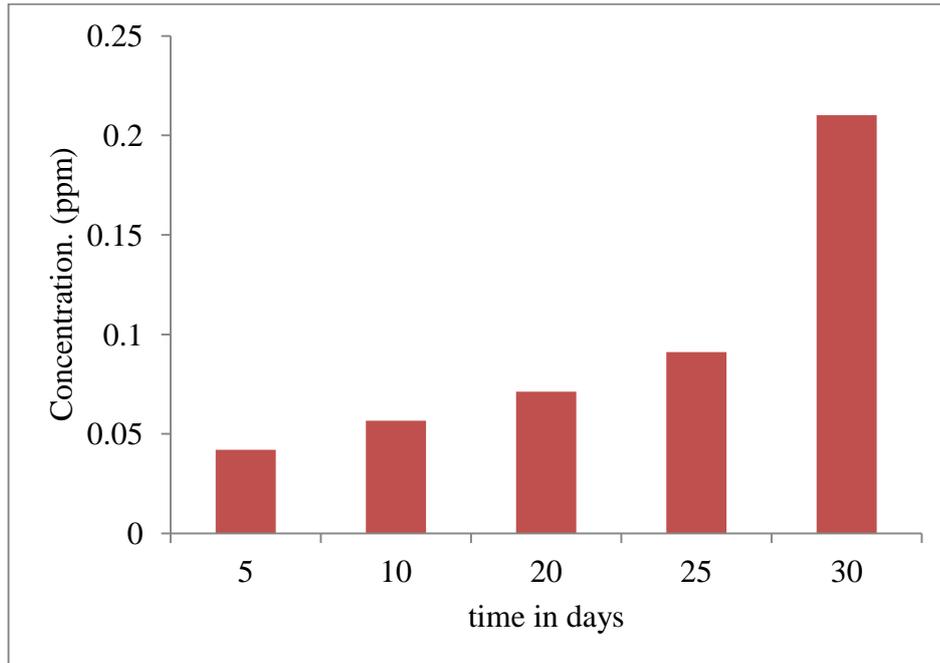


Figure (4.1.c): Plot of concentrations of zinc (Zn^{+2}) in leachate blank water samples.

It is noted from the figures 4.1(b) and 4.1(c), that there is an increase in the concentration of Zn^{+2} in water samples compared with the blank samples. The results also showed that with time there was an increase in the concentrations of Zn^{+2} . This is due to the use of fertilizers which contain heavy metals. Zn^{+2} dissolved in water allowing it to reach the ground water polluting it. The reason is that the organic matter does not block all the spaces among the soil particles, allowing leaching of Zn^{+2} to the ground water.

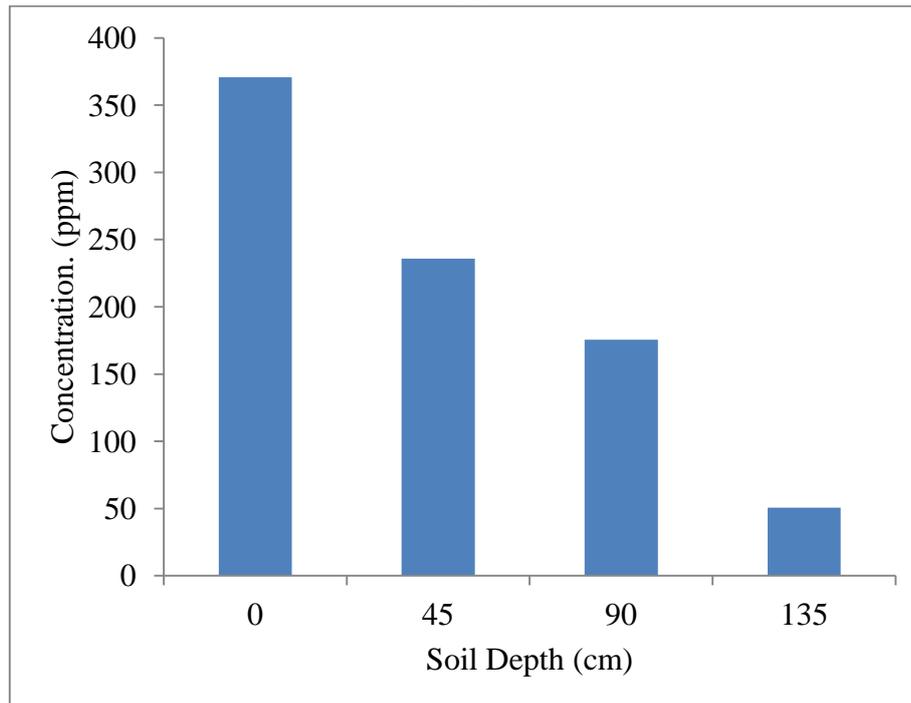


Figure (4.2.a): Plot of concentrations of zinc (Zn²⁺) in fertilized soil samples.

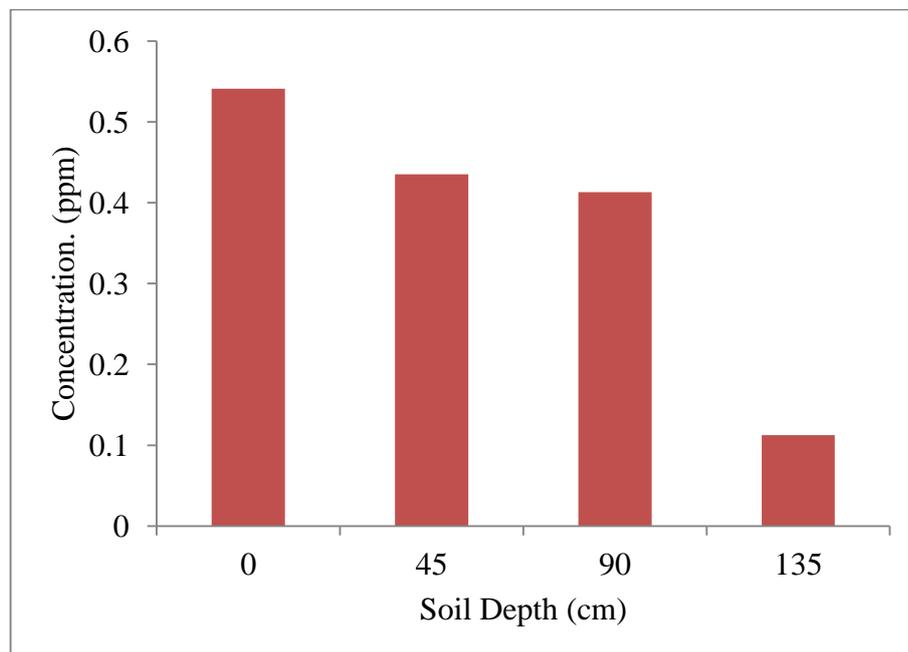


Figure (4.2.b): Plot of concentrations of zinc (Zn²⁺) in blank soil samples.

It is noted from the figures 4.2(a) and 4.2(b), that there is an increase in the concentration of Zn²⁺ in samples of fertilized soil, compared with the blank

samples, due to the use of fertilizers which contains heavy metals. The results also show that with time the concentration of Zn^{+2} decreases in the bottom layer of fertilized soil samples, because it is held by the negative charge of clay soil and adsorbed on the surface of the soil.

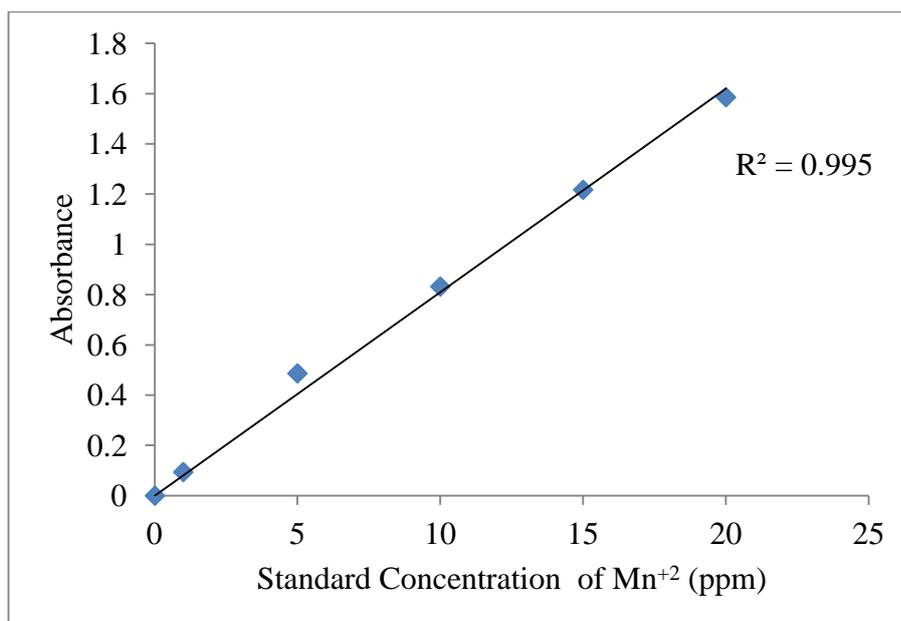


Figure (4.3.a): Calibration curve of manganese (Mn^{+2}).

Stock solution of 1000 ppm of $MnCl_2 \cdot 4H_2O$ was used to prepare different concentrations 1, 5, 10, 15 and 20 ppm, and then the samples were scanned by Flame Atomic Absorption Spectrophotometer. A calibration curve was produced by plotting the absorbance versus Mn^{+2} concentration. The curve is shown in figure 4.3.a. A linear relationship was obtained over the studied concentration range.

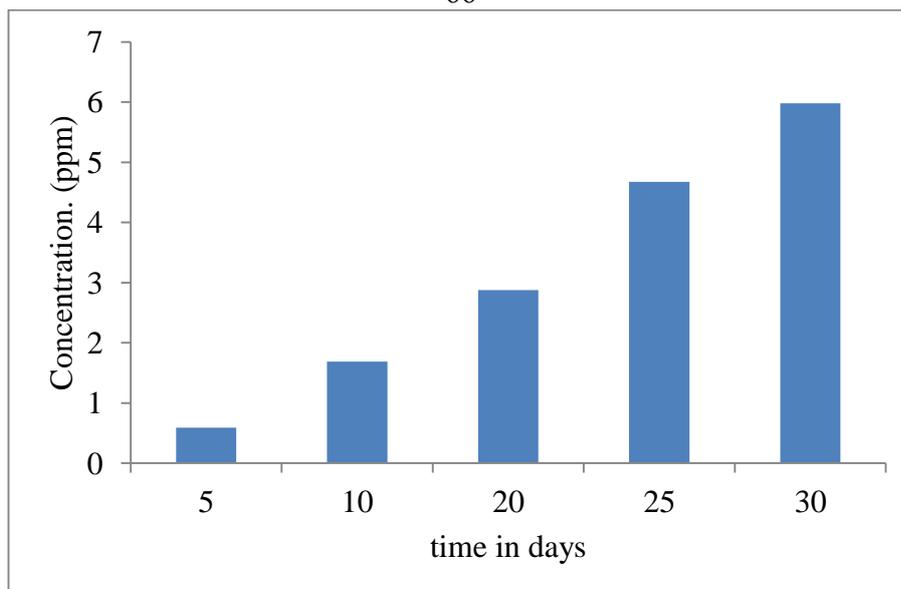


Figure (4.3.b): Plot of concentrations of manganese (Mn^{+2}) in leachate water samples.

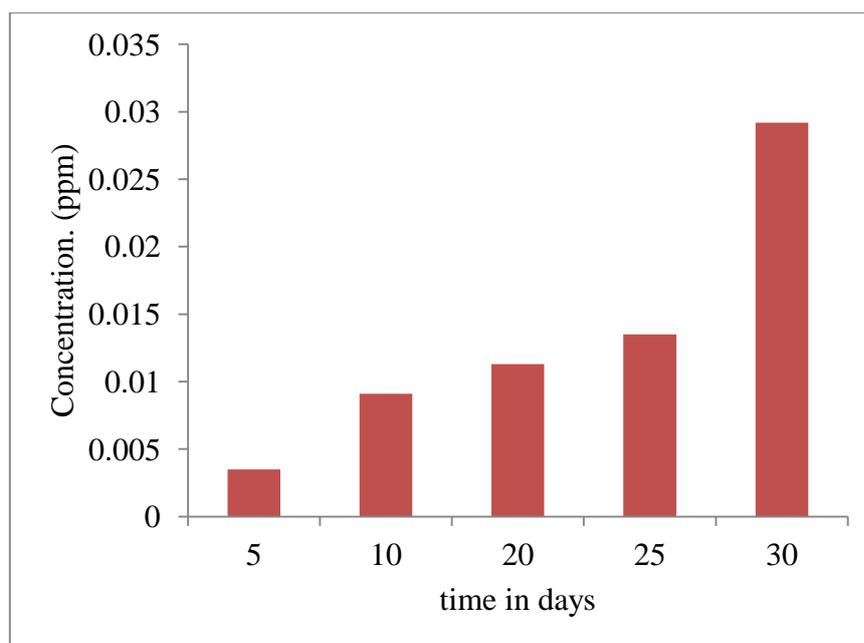


Figure (4.3.c): Plot of concentrations of manganese (Mn^{+2}) in leachate blank water samples.

It is noted from the figures 4.3 (b) and 4.3 (c), that there is an increase in the concentration of Mn^{+2} in water samples compared with the blank samples. The results also show that with time the concentration of Mn^{+2} increases. This is due to the use of fertilizers which contain heavy metals.

Mn^{+2} dissolves in water and reaches to the ground water, polluting it. This is because the organic matter does not block all the space among the soil particles, resulting in leaching of Mn^{+2} into the ground water.

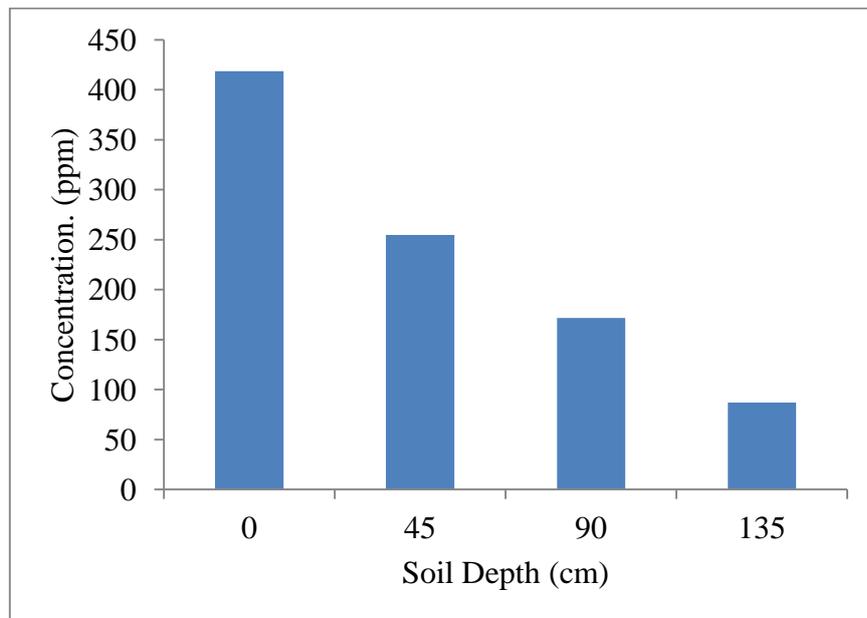


Figure (4.4.a): Plot of concentrations of manganese (Mn^{+2}) in fertilized soil samples.

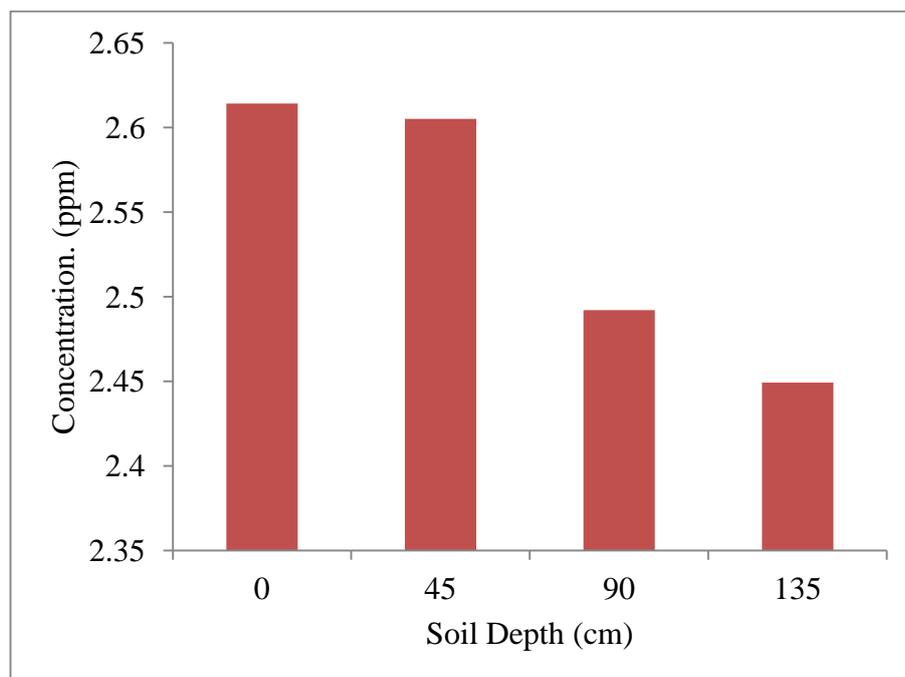


Figure (4.4.b): Plot of concentrations of manganese (Mn^{+2}) in blank soil samples.

It is noted from the figures 4.4(a) and 4.4(b), that there is an increase in the concentration of Mn^{+2} in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contain heavy metals. Also the results show that with time there is a decrease in the concentration of Mn^{+2} in the bottom layer of fertilized soil samples because it is held by the negative charge of clay soil, and adsorbed on the surface of the soil.

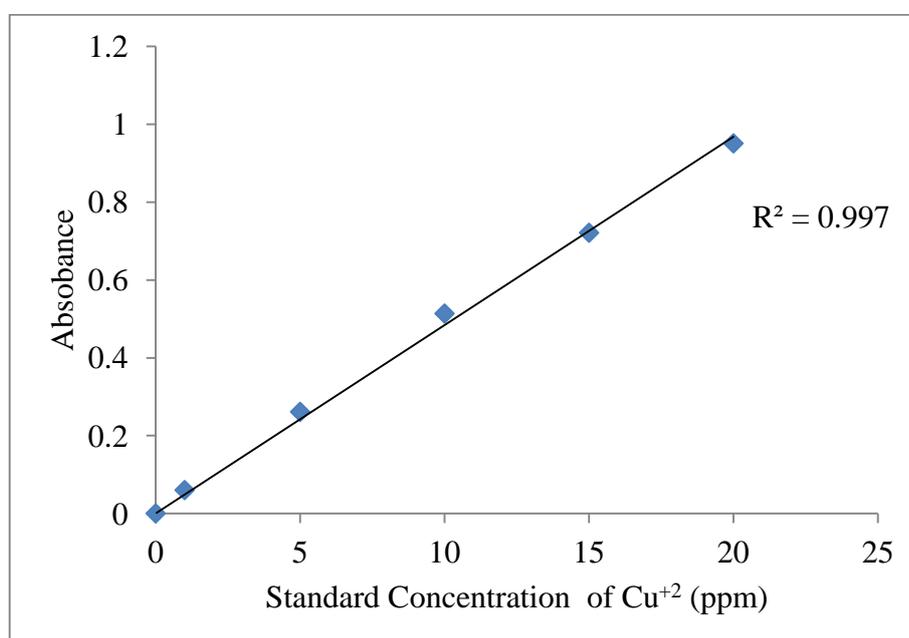


Figure (4.5.a): Calibration curve of copper (Cu^{+2}).

Stock solution of 1000 ppm of CuNO_3 was used to prepare different concentrations 1, 5, 10, 15 and 20 ppm, and then the samples were scanned by Flame Atomic Absorption Spectrophotometer. A calibration curve was produced by plotting the absorbance versus Cu^{+2} concentration. The curve is shown in figure 4.5.a. A linear relationship was obtained over the studied concentration range.

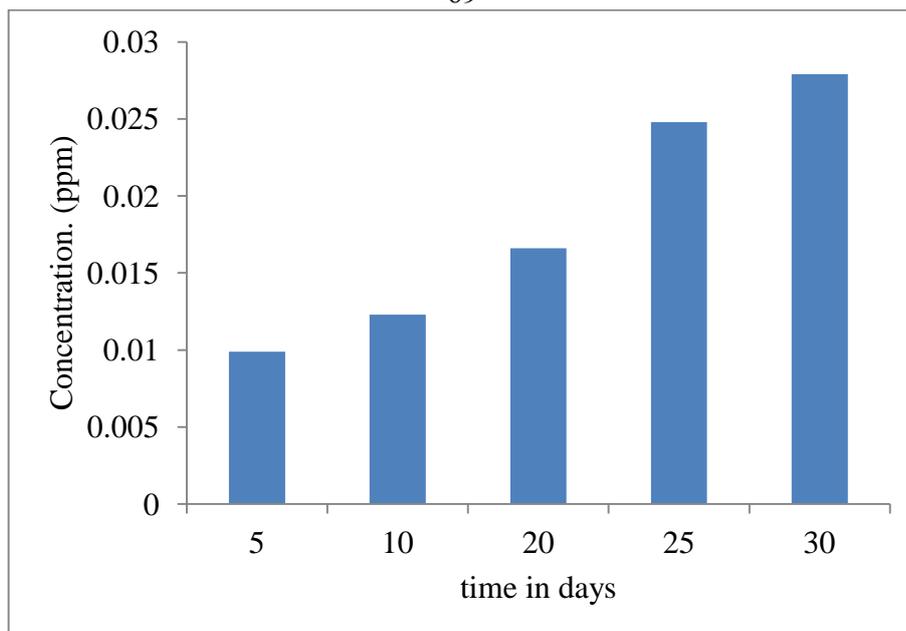


Figure (4.5.b): Plot of concentrations of copper (Cu^{+2}) in leachate water samples.

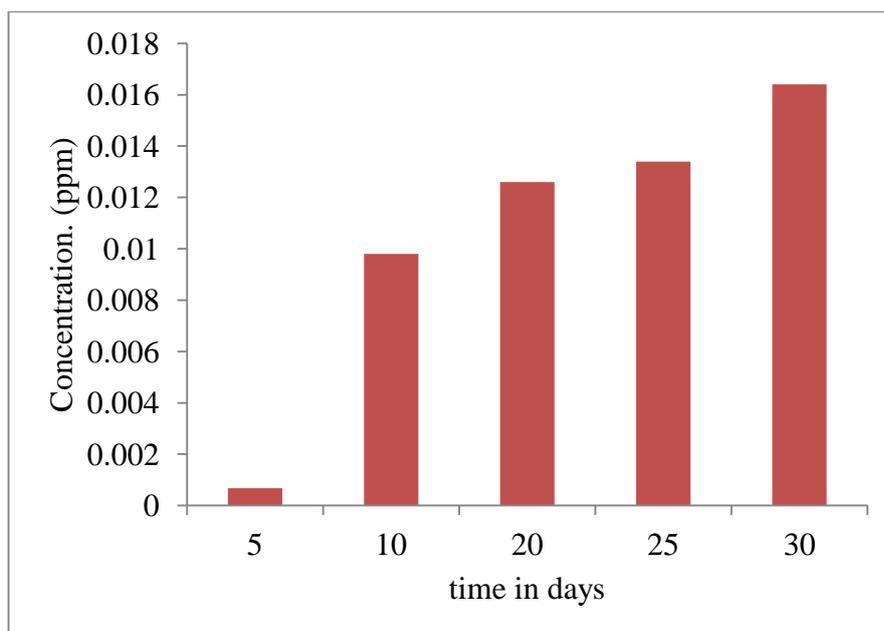


Figure (4.5.c): Plot of concentrations of copper (Cu^{+2}) in leachate blank water samples.

It is noted from the figures 4.5 (b) and 4.5 (c) that there is an increase in the concentration of Cu^{+2} in water samples compared with the blank samples. Results also show that with time there was an increase in the concentration of Cu^{+2} . This is due to the use of fertilizers which contains heavy

metals. Cu^{+2} dissolves in water allowing it to reach the ground water and pollute it. This is because the organic matter does not block all the spaces among the soil particles, allowing leaching of Cu^{+2} to the ground water.

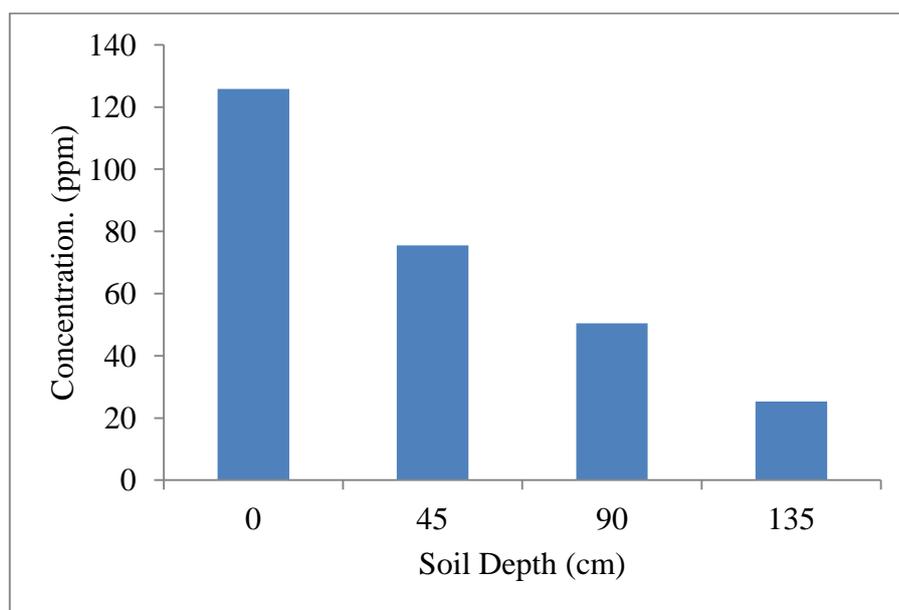


Figure (4.6.a): Plot of concentrations of copper (Cu^{+2}) in fertilized soil samples.

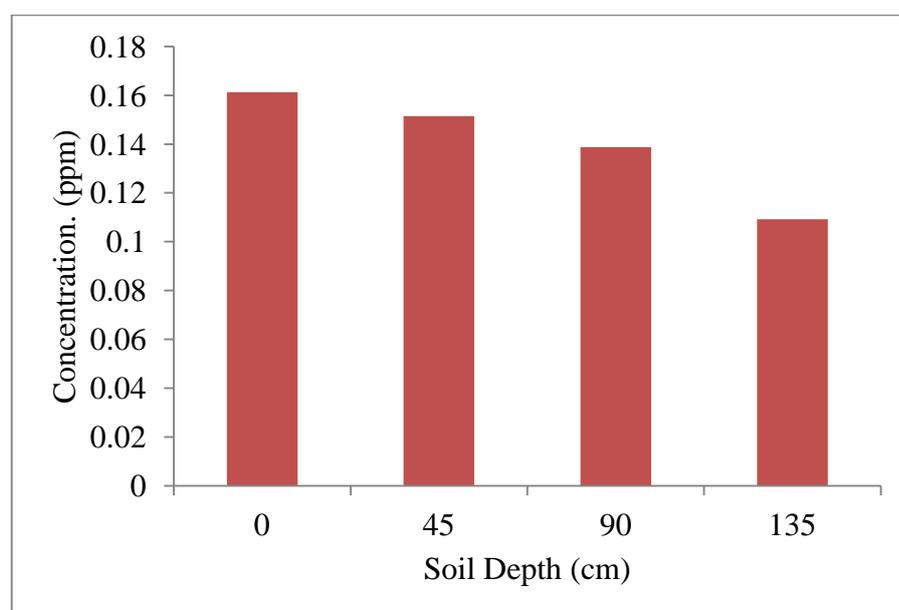


Figure (4.6.b): Plot of concentrations of copper (Cu^{+2}) in blank soil samples.

It is noted from the figures 4.6(a) and 4.6(b), that there is an increase in the concentration of Cu^{+2} in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contains heavy metals. The results also show that with time there is a decrease in the concentration of Cu^{+2} in the bottom layer of fertilized soil samples, because it is held by the negative charge of clay soil, and adsorbed on the surface of the soil.

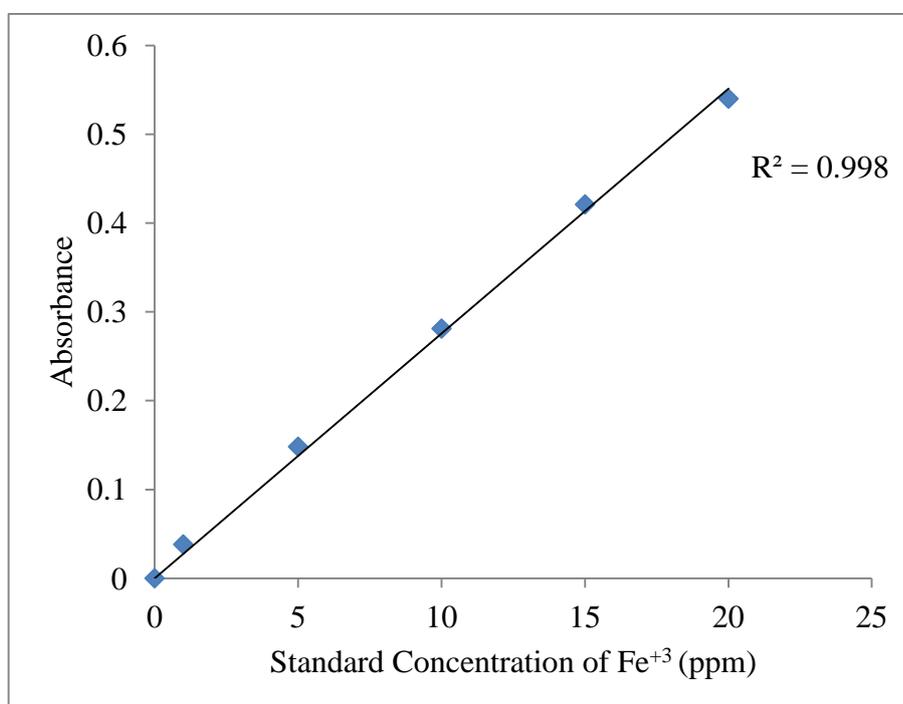


Figure (4.7.a): Calibration curve of iron (Fe^{+3})

Stock solution of 1000 ppm of FeCl_3 was used to prepare different concentrations 1, 5, 10, 15 and 20 ppm, and then the samples were scanned by Flame Atomic Absorption Spectrophotometer. A calibration curve was produced by plotting the absorbance versus Fe^{+3} concentration. The curve is shown in figure 4.7.a. A linear relationship was obtained over the studied concentration range.

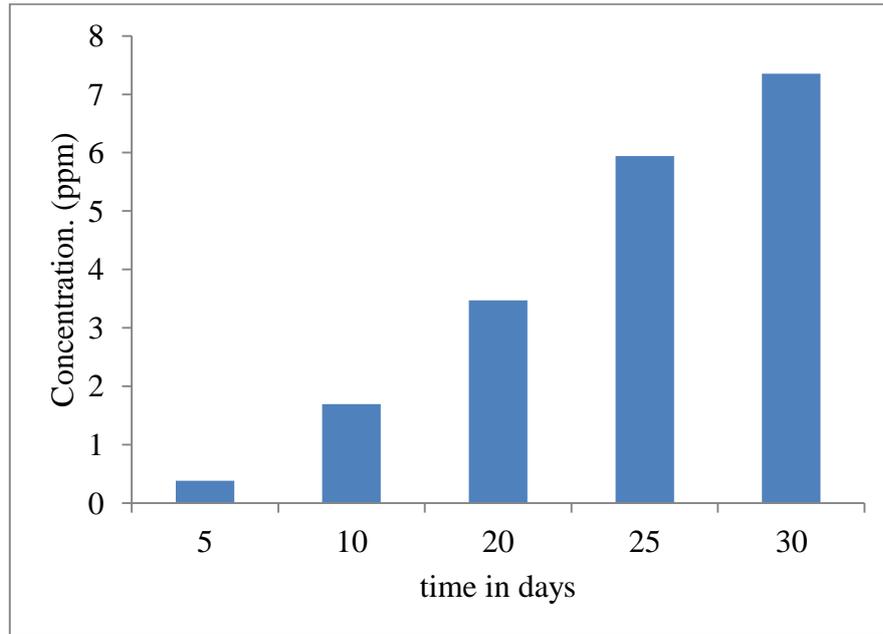


Figure (4.7.b): Plot of concentrations of iron (Fe^{+3}) in leachate water samples.

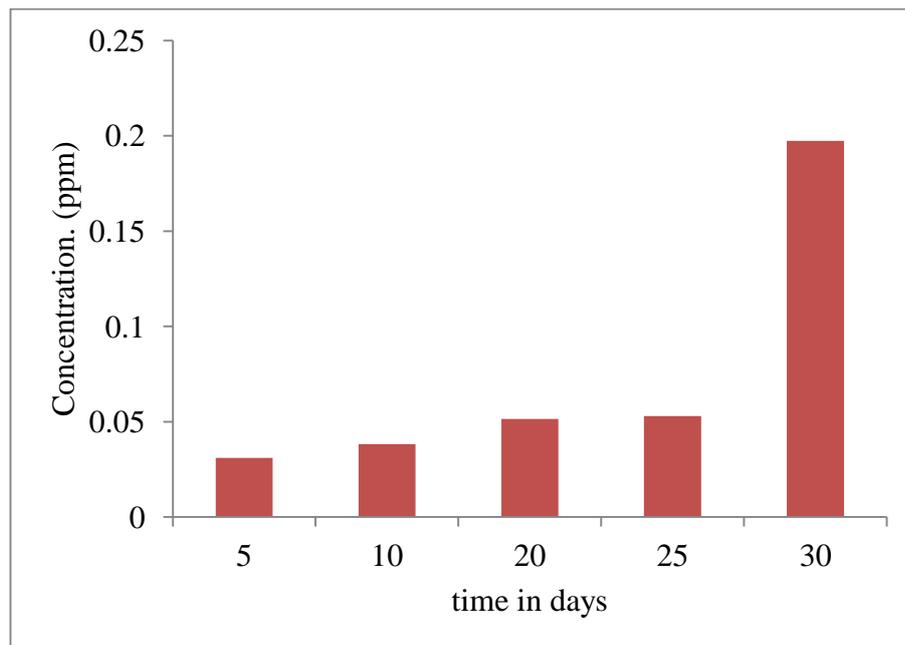


Figure (4.7.c): Plot of concentrations of iron (Fe^{+3}) in leachate blank water samples.

It is noted from the figures 4.7 (b) and 4.7 (c), that there is an increase in the concentration of Fe^{+3} in water samples compared with the blank samples. The results also show that with time, there is an increase in the concentration of Fe^{+3} . This is due to the use of fertilizers which contain

heavy metals. Fe^{+3} dissolves in water to reach the ground water and pollute it. This is because the organic matter does not block all the spaces among the soil particles, leading to leaching of Fe^{+3} to the ground water.

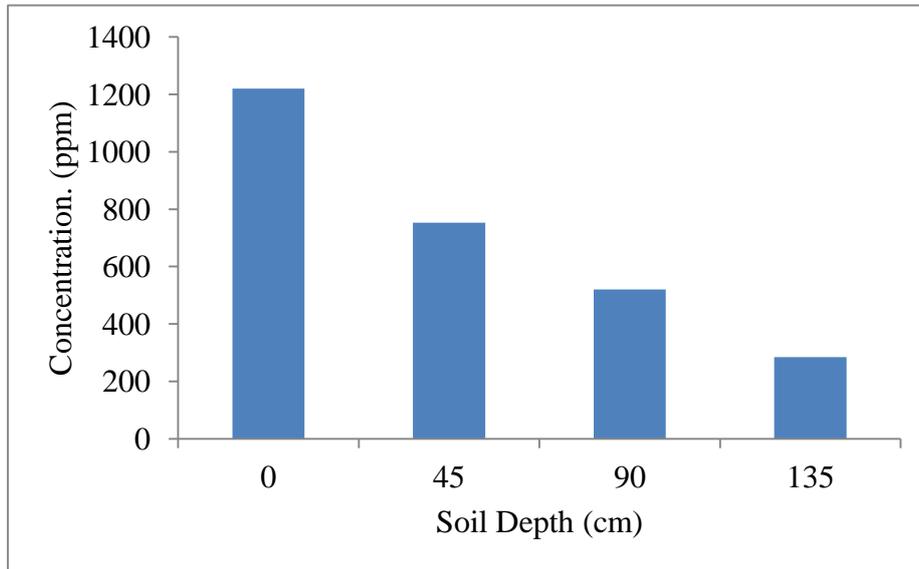


Figure (4.8.a): Plot of concentrations of iron (Fe^{+3}) in fertilized soil samples

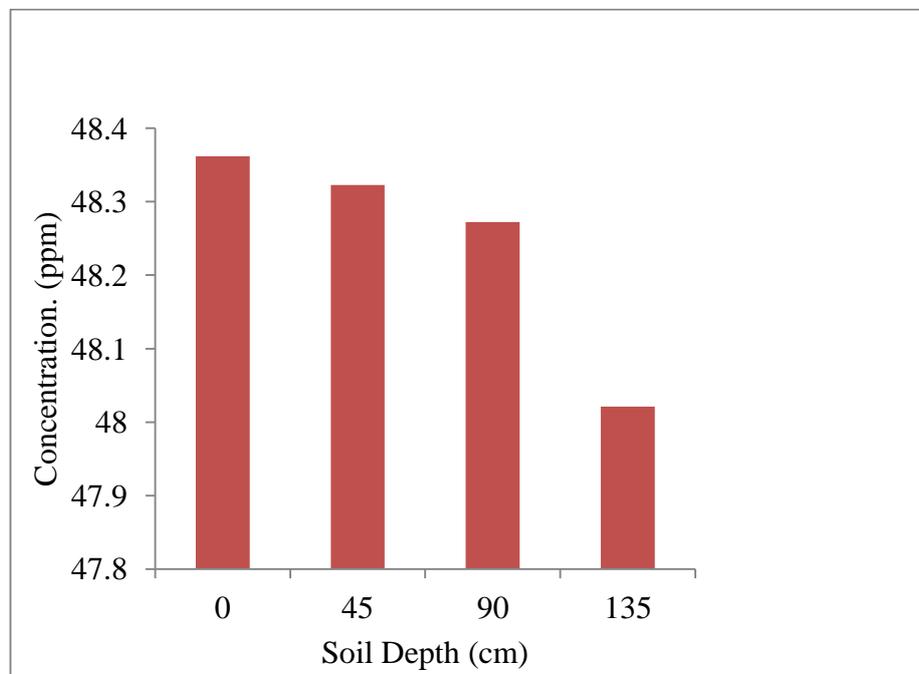


Figure (4.8.b): Plot of concentrations of iron (Fe^{+3}) in blank soil samples

It is noted from the figures 4.8(a) and 4.8(b) that there is an increase in the concentration of Fe^{+3} in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contain heavy metals. The results also show that with time there is a decrease in the concentration of Fe^{+3} in the bottom layer of fertilized soil samples, because it is held by the negative charge of clay soil and adsorbed on the surface of the soil.

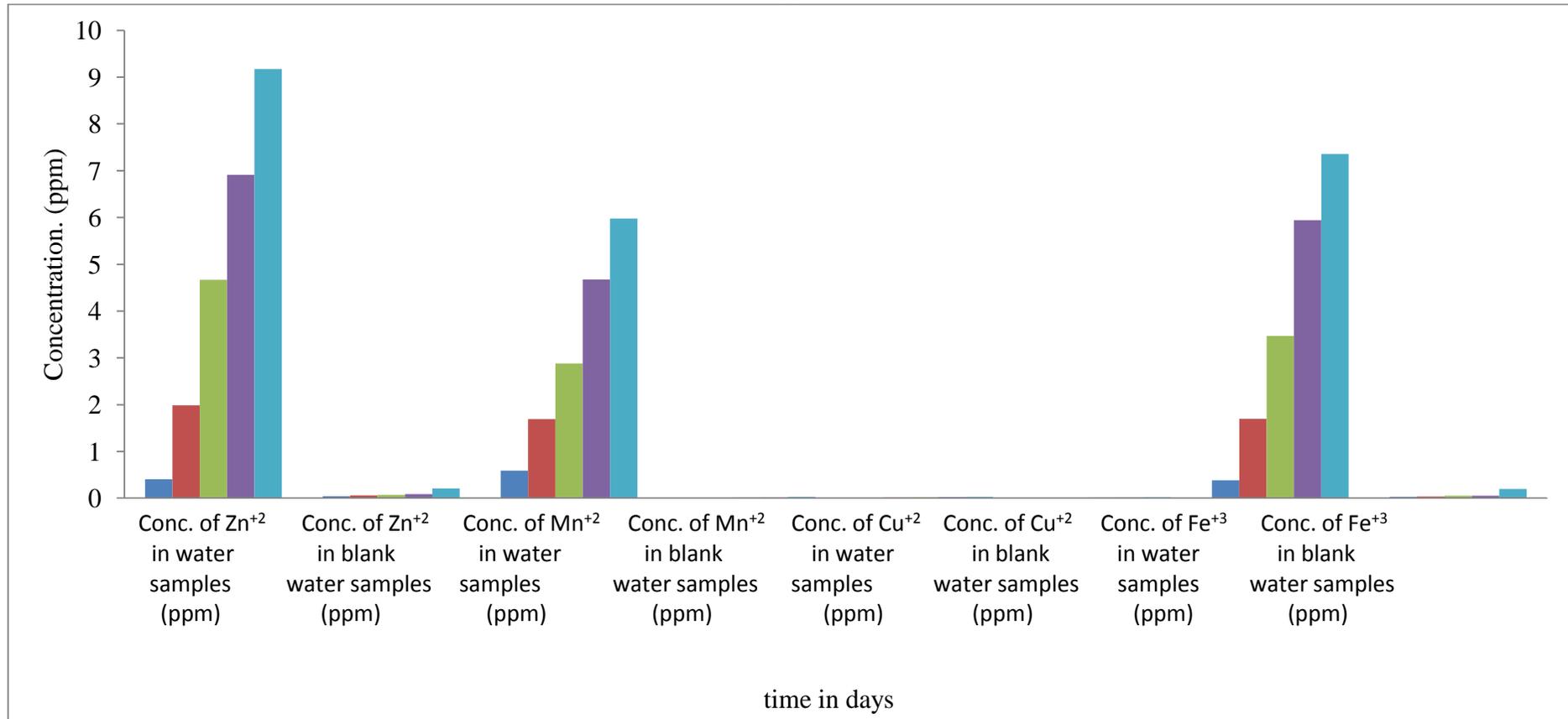


Figure (4.9): Histogram of comparison of the heavy metal concentrations (Zn²⁺, Mn²⁺, Cu²⁺, and Fe³⁺) in leachate blank and water samples.

It is noted from figure (4.9) that there is an increase in the concentration of all heavy metals (Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2}) in the water samples compared with the blank samples. This is due to the use of fertilizers which contains heavy metals. These heavy metals dissolve in water and leachate to the lower layer of soil. The results show that when the concentrations of all heavy metals (Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2}) increase, there is an increase in leachate of the water samples, $\text{Zn}^{+2} > \text{Fe}^{+3} > \text{Mn}^{+2} > \text{Cu}^{+2}$, with means 46 ppm Zn^{+2} , 3.8 ppm Fe^{+3} , 3.2 ppm Mn^{+2} , and 0.02 ppm Cu^{+2} . This means that Zn^{+2} is the most heavy metals that leaches in the ground water than any other heavy metal. It may contaminate the ground water, followed by Fe^{+3} then Mn^{+2} . Cu^{+2} is not leached to the ground water because it is held strongly with clay minerals on the surface of the soil.

It has been observed that the concentration of zinc, iron and manganese ions in water samples were found to be higher than the World Health Organization (WHO) acceptable maximum which is 5mg/L of Zn^{+2} , 0.5mg/L of Fe^{+3} , and 0.5 mg/L of Mn^{+2} . The copper concentration in water samples was lower than the World Health Organization (WHO) acceptable maximum, which is 2mg/L of Cu^{+2} .

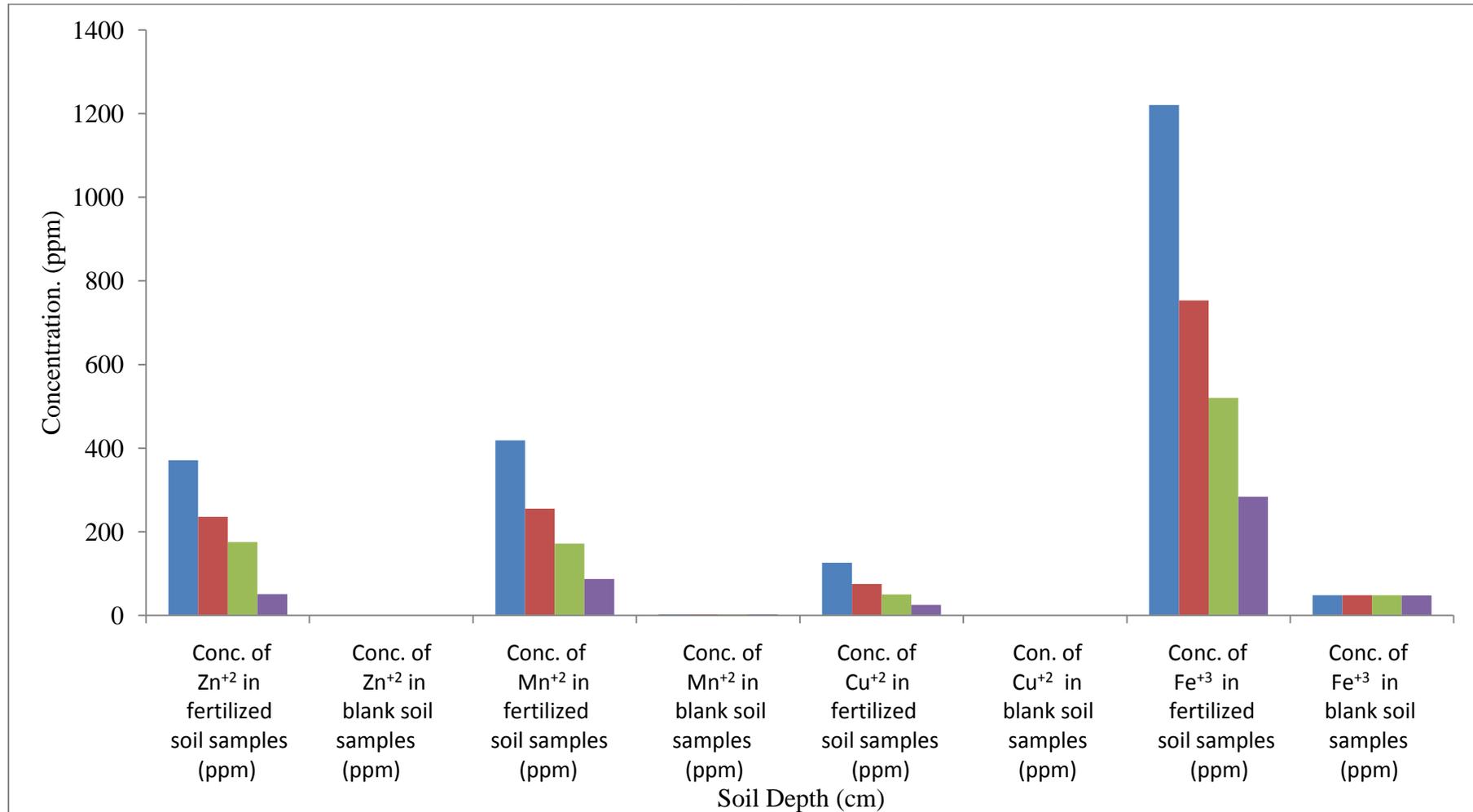


Figure (4.10): Histogram of comparison of the heavy metals concentrations (Zn²⁺, Mn²⁺, Cu²⁺, and Fe³⁺) in blank and fertilized soil samples.

It is noted from figure (4.10) that there is an increase in the concentration of all heavy metals (Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2}) in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contains heavy metals. The results showed that with time, there is a decrease in the concentration of all heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}) in the bottom layer of fertilized soil samples, $\text{Fe}^{+3} > \text{Mn}^{+2} > \text{Zn}^{+2} > \text{Cu}^{+2}$, with means 694.5 ppm Fe^{+3} , 233.1 ppm Mn^{+2} , 208.2 ppm Zn^{+2} , and 69.2 ppm Cu^{+2} . This means that Fe^{+3} is the most heavy metal that accumulates in the soil than the other heavy metals, followed by Mn^{+2} , Zn^{+2} , and Cu^{+2} . The accumulation of Cu^{+2} in the soil is not dangerous to the environment due to its stable compound in the soil, but the accumulation of Zn^{+2} in the soil was toxic. The excessive application of fertilizers that contain heavy metals as Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2} for agricultural purposes, may form risks to humans and cause health problems. It may pose hazards to the ecosystem: the food chain, water, animals and plants. The long term use of fertilizers leads to accumulation of heavy metals as Fe^{+3} , Cu^{+2} , Mn^{+2} , and Zn^{+2} in soils in toxic levels.

It has been observed that the concentration of both iron and manganese in fertilized soil follows the World Health Organization (WHO) acceptable maximum. The World Health Organization (WHO) acceptable maximum of the previous metals is the following: 2000 ppm of Mn^{+2} and 38000 ppm of Fe^{+3} , while copper and zinc ion concentrations were found to be higher than the World Health Organization (WHO), where the acceptable maximum is 100 ppm of Cu^{+2} , and 300 ppm of Zn^{+2} .

4.3. Determination of the concentration for some Nutrients:

To determine the concentrations of three nutrients (K_2O , NO_3^- , P_2O_5) in nine samples of soil (one before fertilization and eight after fertilization), ten samples of water which leachate from the fertilized soil, and one sample of compound fertilizer. The results are represented in Table (4.3).

Table (4.3): Nitrate, phosphorus, and potassium concentrations in nine samples of soil, ten samples of water which leachate from the fertilized soil, and one sample of compound fertilizer.

Name of Sample	NO_3^- con. (ppm)	P_2O_5 con. (ppm)	K_2O con. (ppm)
11 (water)	81.5	0.192857	0.1344
12 (water)	172	0.3	0.2022
13 (water)	1302	0.521429	0.3622
14 (water)	3224	0.65	0.4444
15 (water)	4800	0.885714	0.5333
Mean	1915.9	0.51	0.34
21 (blank) (water)	0.01	0.164286	0.133
22 (blank) (water)	0.016	0.207143	0.189
23 (blank) (water)	0.123	0.228571	0.256
24 (blank) (water)	0.142	0.2643	0.289
25 (blank) (water)	0.184	0.3071	0.322
Mean	0.095	0.23	0.24
WHO Standards	45	0.4 – 0.5	10-12
1A0 (soil)	59.78	207.8643	158.6556
1AB45 (soil)	91.96	201.7286	157.544
1BC90 (soil)	110.77	4.0929	90.878
1C135 (soil)	158.38	0.3357	35.989
Mean	105.2	103.5	110.8
2A0 (blank) (soil)	0	34.2643	3.311
2AB45 (blank) (soil)	0	24.3429	1.833
2 BC90 (blank) (soil)	0	1.557	0.322
2 C135 (blank) (soil)	0	0.1929	0.134
Mean	0	15.1	1.4
The red soil before fertilizer	0.48	62.01429	6.789
Compound fertilizer sample	2000	70.95714	87.6

It is noted from the table 4.3 that there is an increase in the concentration of all nutrients (NO_3^- , P_2O_5 and K_2O) in water samples compared with the blank samples. This is due to the use of fertilizers which contain nutrients. The results show that when there is an increase in the concentration of nutrients (NO_3^- , P_2O_5 and K_2O) there is an increase in the leachate of water samples, $\text{NO}_3^- > \text{P}_2\text{O}_5 > \text{K}_2\text{O}$, with means 1915,9 ppm NO_3^- , 0.51 ppm P_2O_5 and 0.34 ppm K_2O . NO_3^- due to its negative charge is not held by the negative charge of clay minerals, so it is the most nutrient that is leached in the ground water than the other nutrients. It may contaminate the ground water. This is followed by P_2O_5 , which leaches less due to the formation of complexes with the soil. Finally, K_2O due to its positive charge, is held by the negative charge of clay minerals.

It has been observed that the concentrations of both nitrogen as nitrate and phosphorus in water samples were found to be higher than the World Health Organization (WHO) acceptable maximums, which are 45mg/L for NO_3^- , and 5 mg/L for P_2O_5 , while the concentration of potassium in the water samples was found to be lower than World Health Organization (WHO) standards, where the acceptable maximum is 10-12 mg/L for K_2O . This means that P_2O_5 and NO_3^- leached in the ground water and contaminated it.

Also, it is noted from the table 4.3 that there is an increase in the concentration of all nutrients (NO_3^- , P_2O_5 and K_2O) in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contain nutrients. The results show that with time the concentration of NO_3^- increases, while the concentration of P_2O_5 and K_2O decreases in the bottom layer of the soil, $\text{K}_2\text{O} > \text{P}_2\text{O}_5 > \text{NO}_3^-$, with means 110.8 ppm

K_2O , 103.5 ppm P_2O_5 and 105.2 ppm NO_3^- . This means that K_2O is the most nutrient that accumulates in and on the soil compared to the other nutrients, followed by P_2O_5 , and finally NO_3^- .

K_2O accumulation is mainly on the surface of the soil because it makes complex compounds with organic matter, followed by NO_3^- , finally P_2O_5 .

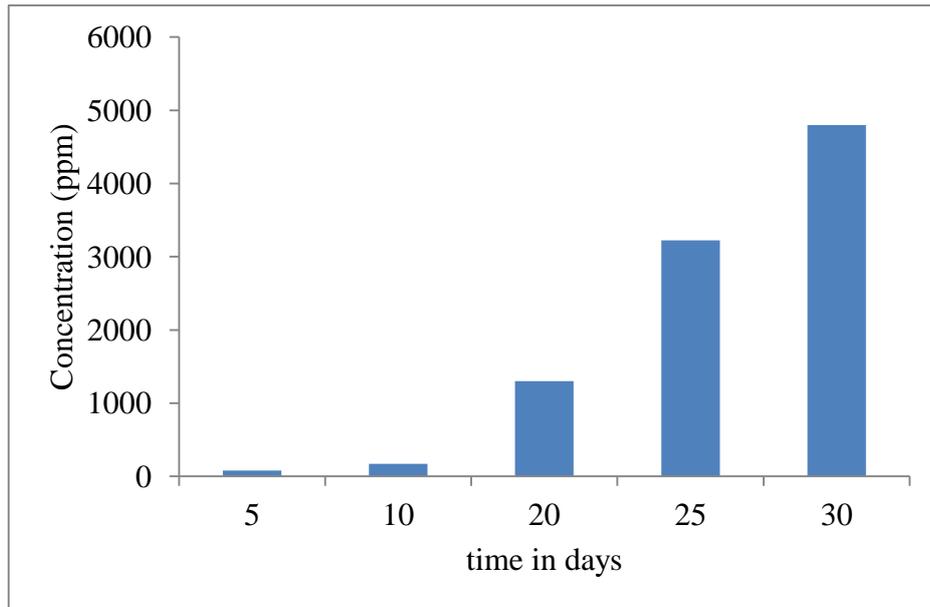


Figure (4.11.a): Plot of concentrations of nitrate (NO_3^-) in leachate water samples.

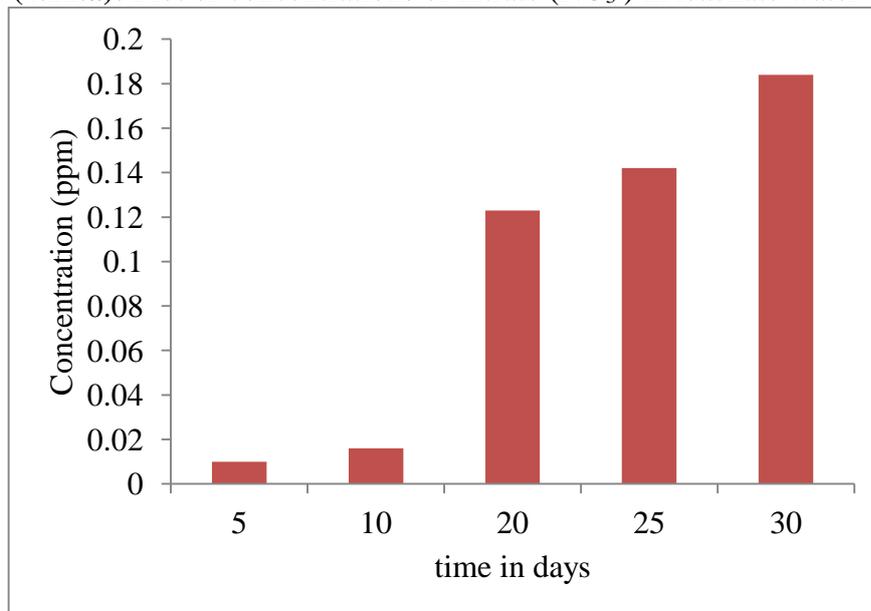


Figure (4.11.b): Plot of concentrations of nitrate (NO_3^-) in leachate blank water samples.

It is noted from the figures 4.11(a) and 4.11(b), that there is an increase in the concentration of NO_3^- in water samples compared with the blank samples. The results also show that with time the concentration of NO_3^- increases in the leachate of water samples. This is due to the use of fertilizers which contain nutrients, and because nitrate has a negative charge that does not allow it to bind with the negative charge of clay soil. So the nitrate ions leach to the ground water.

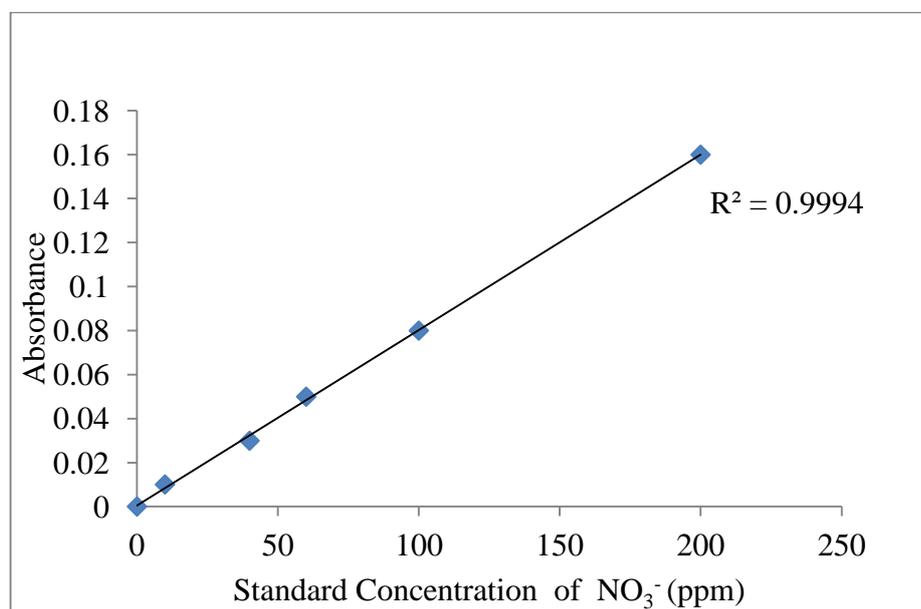


Figure (4.12.a): Calibration curve of nitrate (NO_3^-) at 410 nm

Stock solution of 15000 ppm of KCl was used to prepare different concentrations 10, 40, 60, 100 and 200 ppm, and then the samples were scanned by UV spectrophotometer. A calibration curve was produced by plotting the absorbance (measured at 410 nm) versus NO_3^- concentration. The curve is shown in figure 4.12.a. A linear relationship was obtained over the studied concentration range.

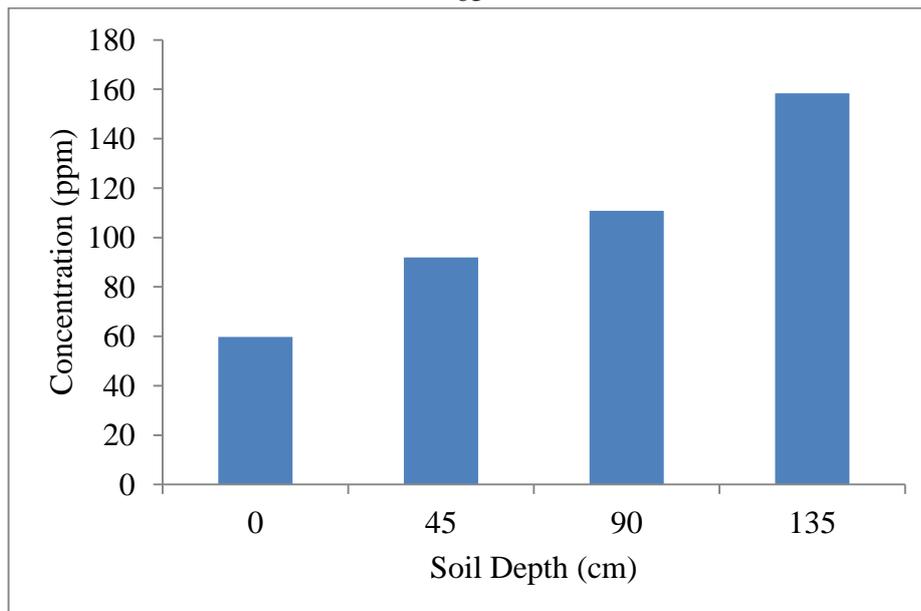


Figure (4.12.b): Plot of concentrations of nitrate (NO₃⁻) in fertilized soil samples.

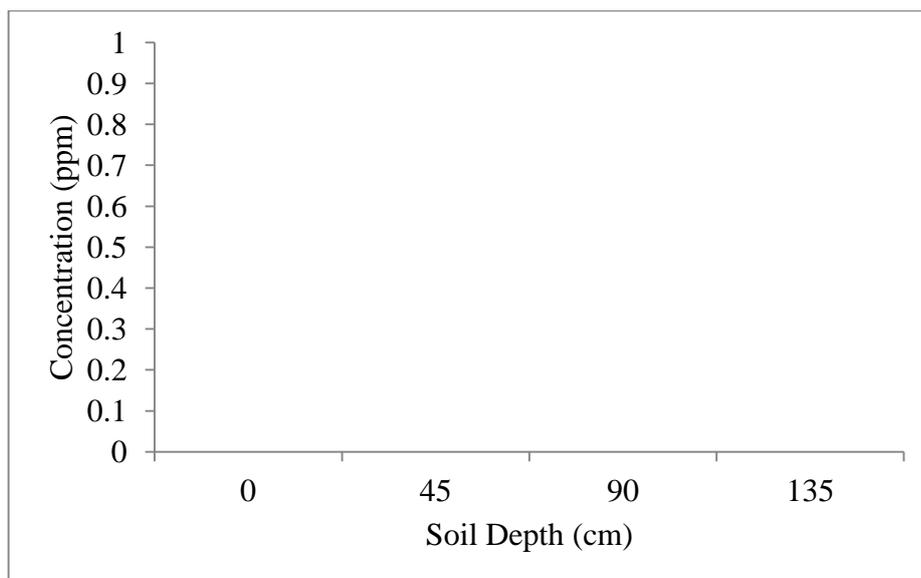


Figure (4.12.c): Plot of concentrations of nitrate (NO₃⁻) in blank soil samples.

It is noted from the figure 4.12 (b) and 4.12 (c) there is an increase in the concentration of NO₃⁻ in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contains nutrients. Also, the results show that with time the concentration of NO₃⁻ increases in the

bottom layer of the soil, because NO_3^- is not held by the clay minerals on the surface of the soil.

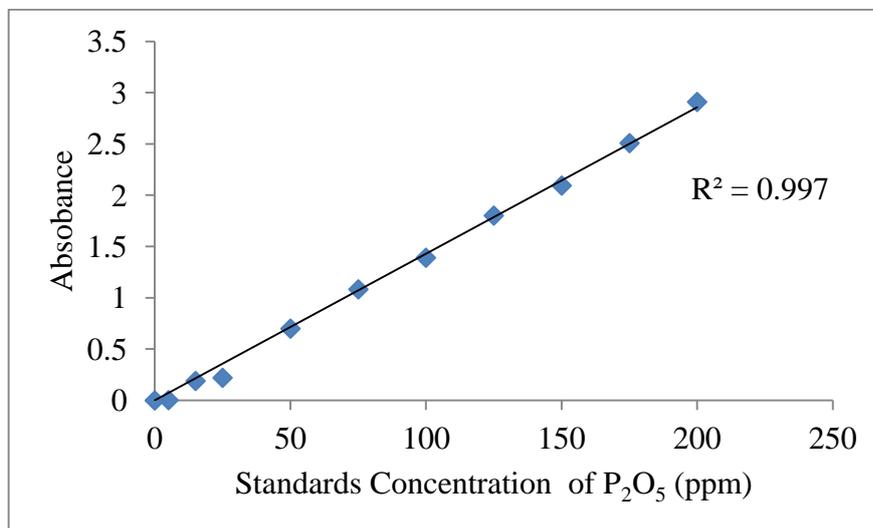


Figure (4.13.a): Calibration curve of phosphorus as P_2O_5 at 840 nm

Stock solution of 1434 ppm of KH_2PO_4 was used to prepare different concentrations 5, 10, 15, 25, 50, 75, 100, 125, 150, 175 and 200 ppm, and then the samples were scanned by UV spectrophotometer. A calibration curve was produced by plotting the absorbance (measured at 840 nm) versus P_2O_5 concentration. The curve is shown in figure 4.13.a. A linear relationship was obtained over the studied concentration range.

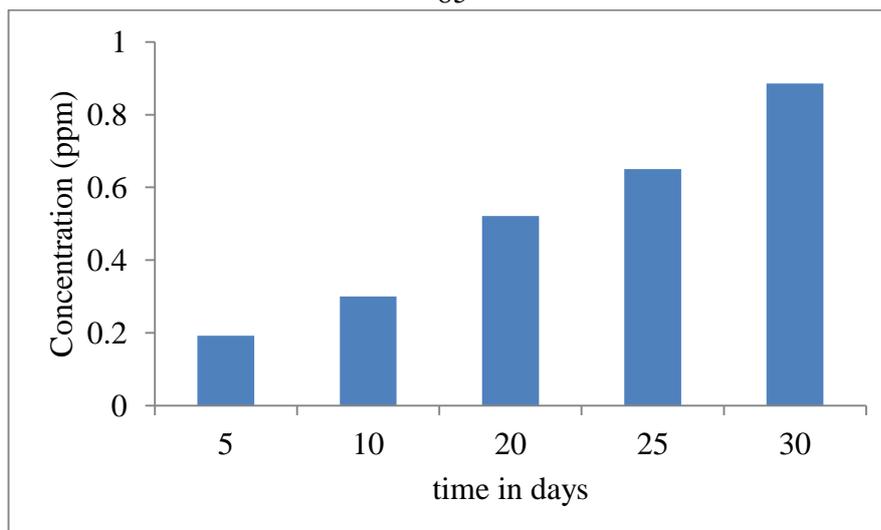


Figure (4.13.b): Plot of concentrations of phosphorus as P_2O_5 in leachate water samples.

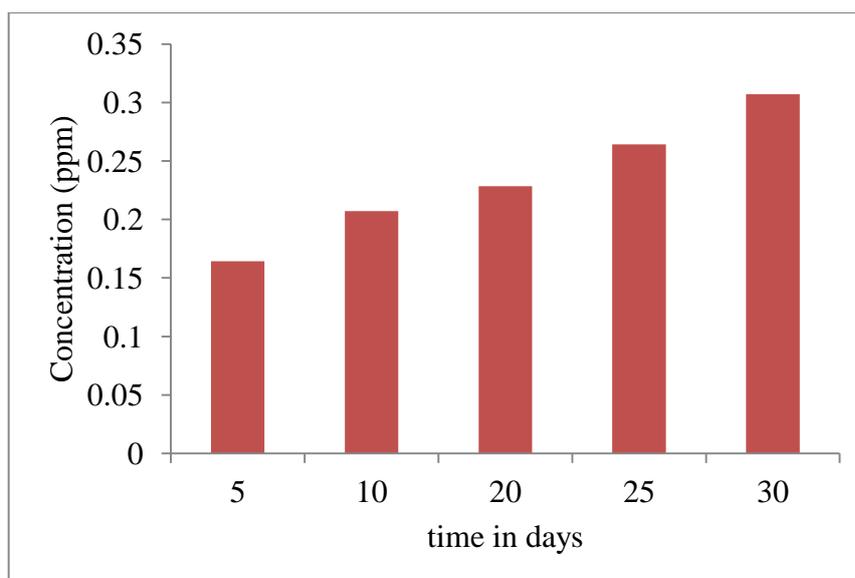


Figure (4.13.c): Plot of concentrations of phosphorus as P_2O_5 in leachate blank water samples.

It is noted from the figures 4.13 (b) and 4.13 (c), that there is an increase in the concentration of P_2O_5 in water samples compared with the blank samples. Also the results show that with time the concentration of P_2O_5 increases in the leachate of water samples. This is due to the use of

fertilizers which contain nutrients, and because the organic matter does not block all the spaces among the soil particles, resulting in leaching of P_2O_5 into the ground water.

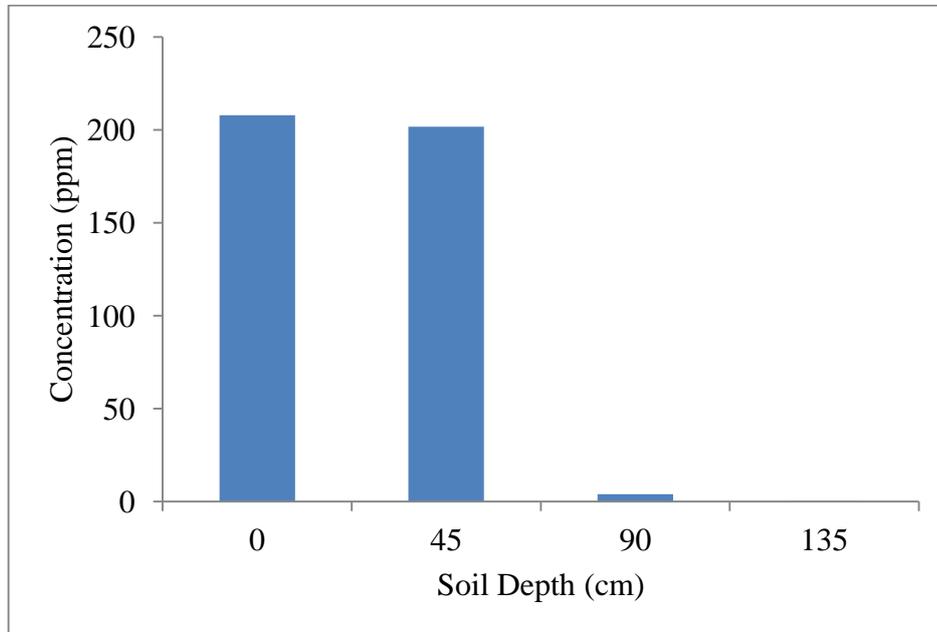


Figure (4.14.a): Plot of concentrations of phosphorus as P_2O_5 in fertilized soil samples.

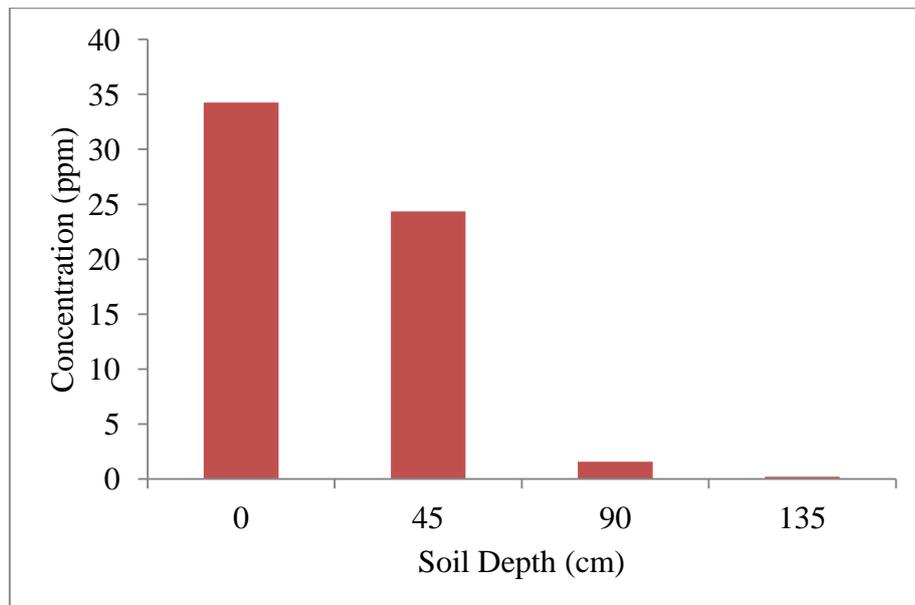


Figure (4.14.b): Plot of concentrations of phosphorus as P_2O_5 in blank soil samples.

It is noted from the figures 4.14 (a) and 4.14 (b) that there is an increase in the concentration of P_2O_5 in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contain nutrients. Also, the results show that with time the concentration of P_2O_5 decreases in the bottom layer of the soil, because P_2O_5 is held by the clay minerals and make complexes. They also adsorb on the surface of the soil.

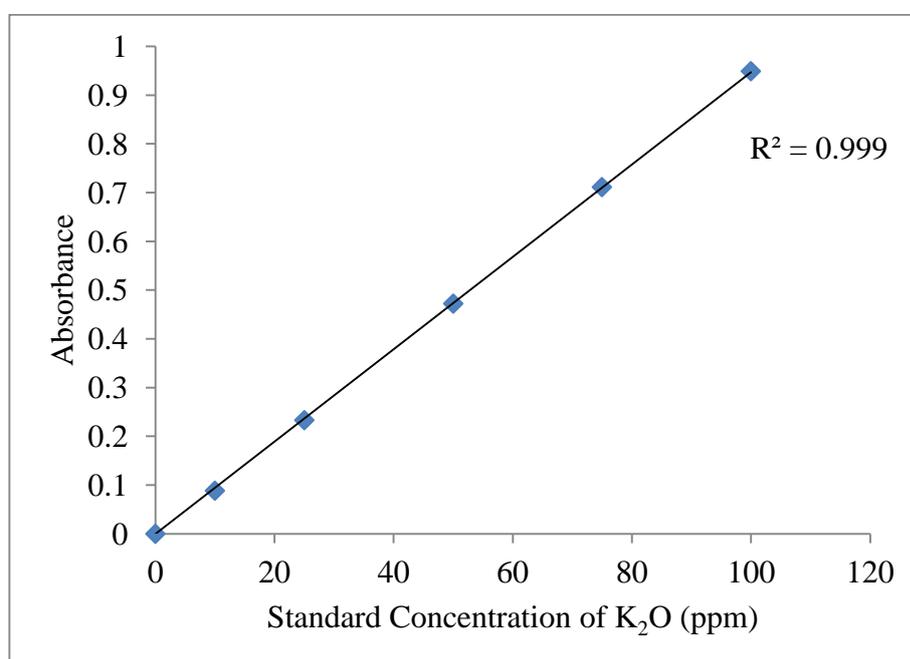


Figure (4.15.a): Calibration curve of potassium as K_2O at 234 nm.

Stock solution of 1000 ppm of KNO_3 was used to prepare different concentrations 10, 25, 50, 75 and 100 ppm, and then the samples were scanned by UV spectrophotometer. A calibration curve was produced by plotting the absorbance (measured at 234 nm) versus K_2O concentration. The curve is shown in figure 4.15.a. A linear relationship was obtained over the studied concentration range.

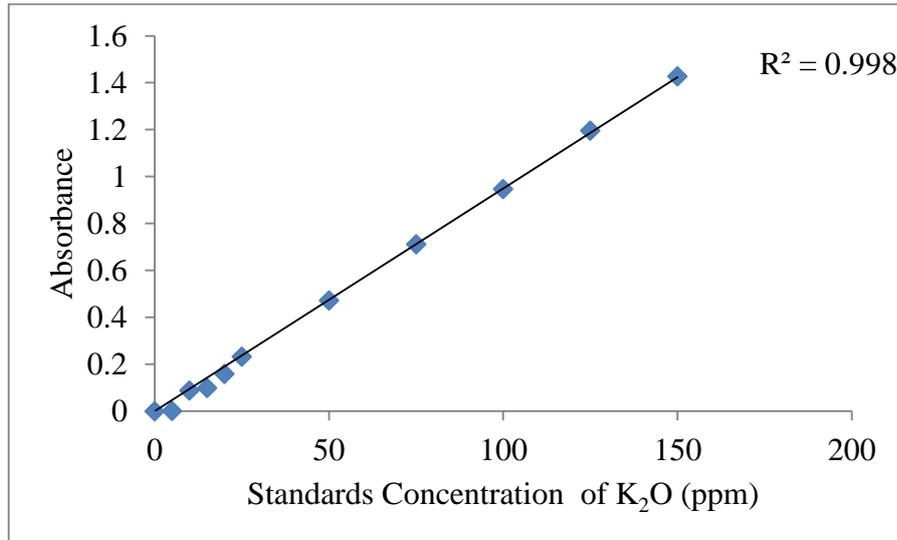


Figure (4.15.b): Calibration curve of potassium as K₂O at 234 nm.

Stock solution of 1000 ppm of KNO₃ was used to prepare different concentrations 5, 10, 15, 20, 25, 50, 75, 100, 125 and 150 ppm, and then the samples were scanned by UV spectrophotometer. A calibration curve was produced by plotting the absorbance (measured at 234 nm) versus K₂O concentration. The curve is shown in figure 4.15.b. A linear relationship was obtained over the studied concentration range.

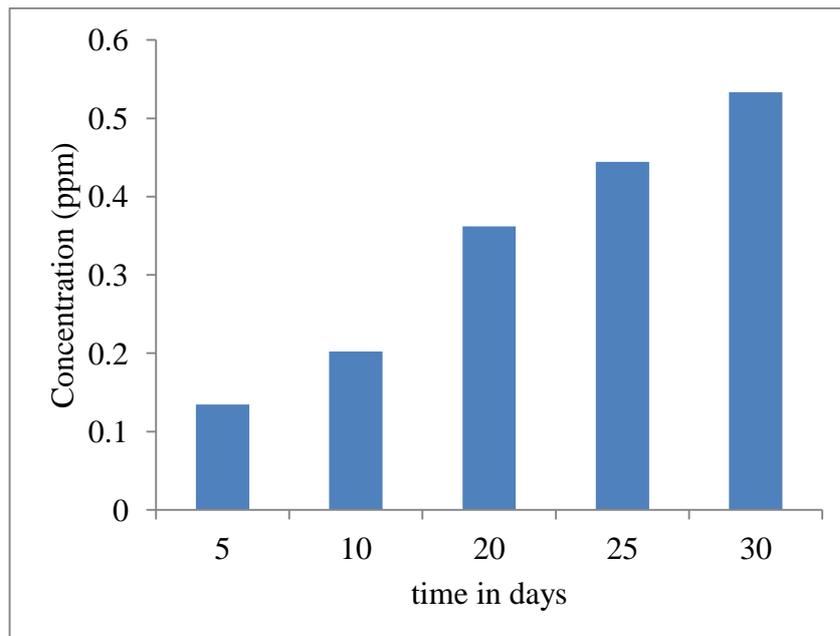


Figure (4.16.a): Plot of concentrations of potassium as K₂O in leachate water samples.

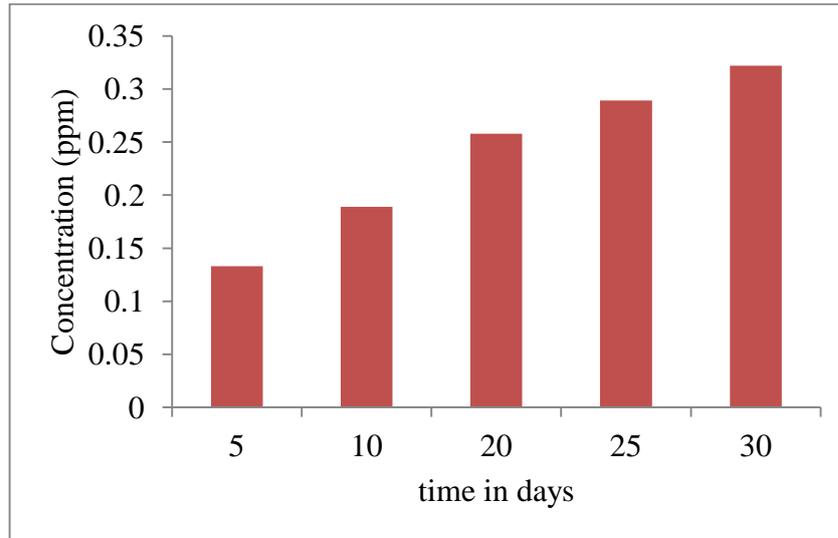


Figure (4.16.b): Plot of concentrations of potassium as K_2O in leachate blank water samples.

It is noted from the figures 4.16 (a) and 4.16 (b) that there is an increase in the concentration of K_2O in water samples compared with the blank samples. Also, the results show that with time the concentration of K_2O increases in the leachate of water samples. This is due to the use of fertilizers which contain nutrients, and because the organic matter does not block all the spaces among the soil particles, resulting in leaching of K_2O into the ground water.

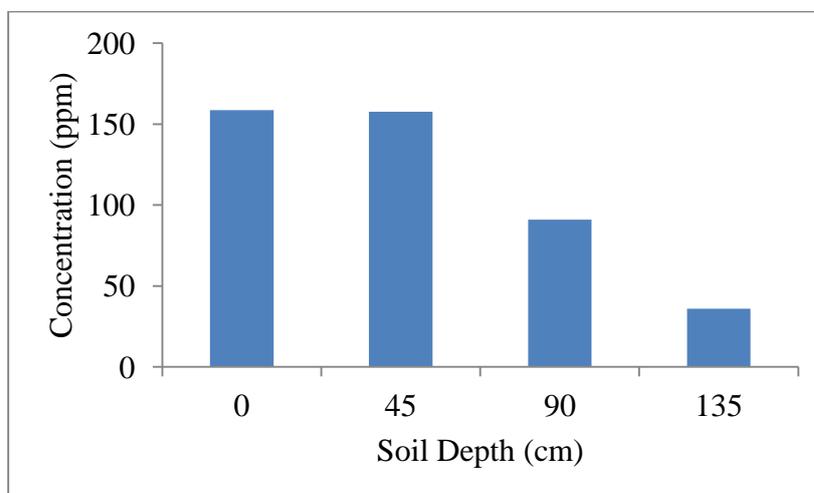


Figure (4.17.a): Plot of concentrations of potassium as K_2O in fertilized soil samples

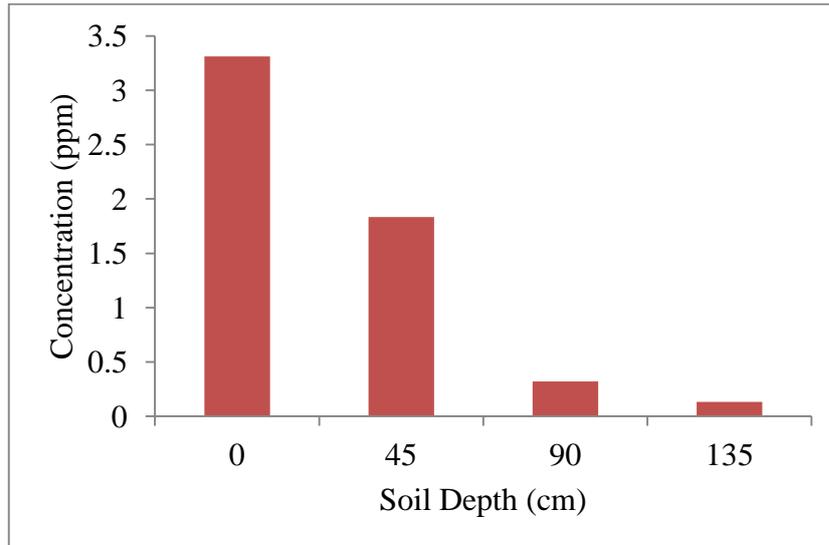


Figure (4.17.b): Plot of concentrations of potassium as K_2O in blank soil samples.

It is noted from the figures 4.17 (a) and 4.17 (b) that there is an increase in the concentration of K_2O in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contain nutrients. Also, the results show that with time the concentration of K_2O decreases in the bottom layer of the soil, because K_2O has a positive charge and is held by the negative charge of clay soil, causing it to be adsorbed on the surface of the soil.

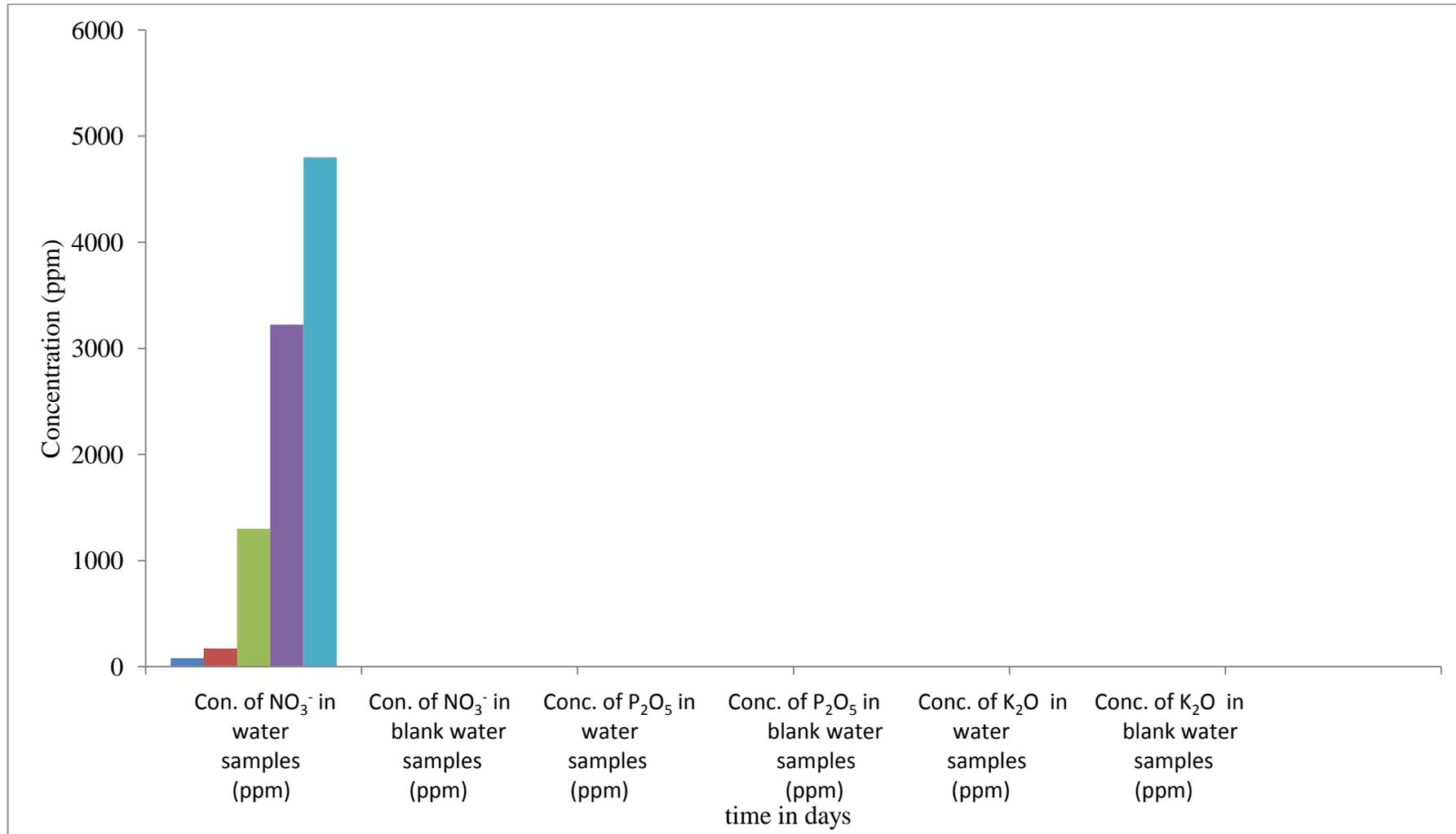


Figure (4.18.a): Histogram of comparison of the nutrients concentrations (NO₃⁻, P₂O₅ and K₂O) in leachate blank and water samples.

It is noted from the figures 4.18.(a) that there is an increase in the concentration of all nutrients (NO_3^- , P_2O_5 and K_2O) in water samples compared with the blank samples. This is due to the use of fertilizers which contain nutrients. The results show that when there is an increase in the concentration of nutrients (NO_3^- , P_2O_5 and K_2O), there is an increase in the leachate of water samples, $\text{NO}_3^- > \text{P}_2\text{O}_5 > \text{K}_2\text{O}$, with means 1915,9 ppm NO_3^- , 0.51 ppm P_2O_5 and 0.34 ppm K_2O . This means that NO_3^- is the most nutrient that leached in the ground water compared to the other nutrients. Allowing it to contaminate the ground water.

It has been observed that the concentrations of both nitrogen as nitrate and phosphorus in water samples were found to be higher than the World Health Organization (WHO) where the acceptable maximum is 45mg/L for NO_3^- , and 5 mg/L for P_2O_5 , while the concentration of potassium in the water samples was found to be lower than World Health Organization (WHO) standards, where the acceptable maximum is 10-12 mg/L for K_2O .

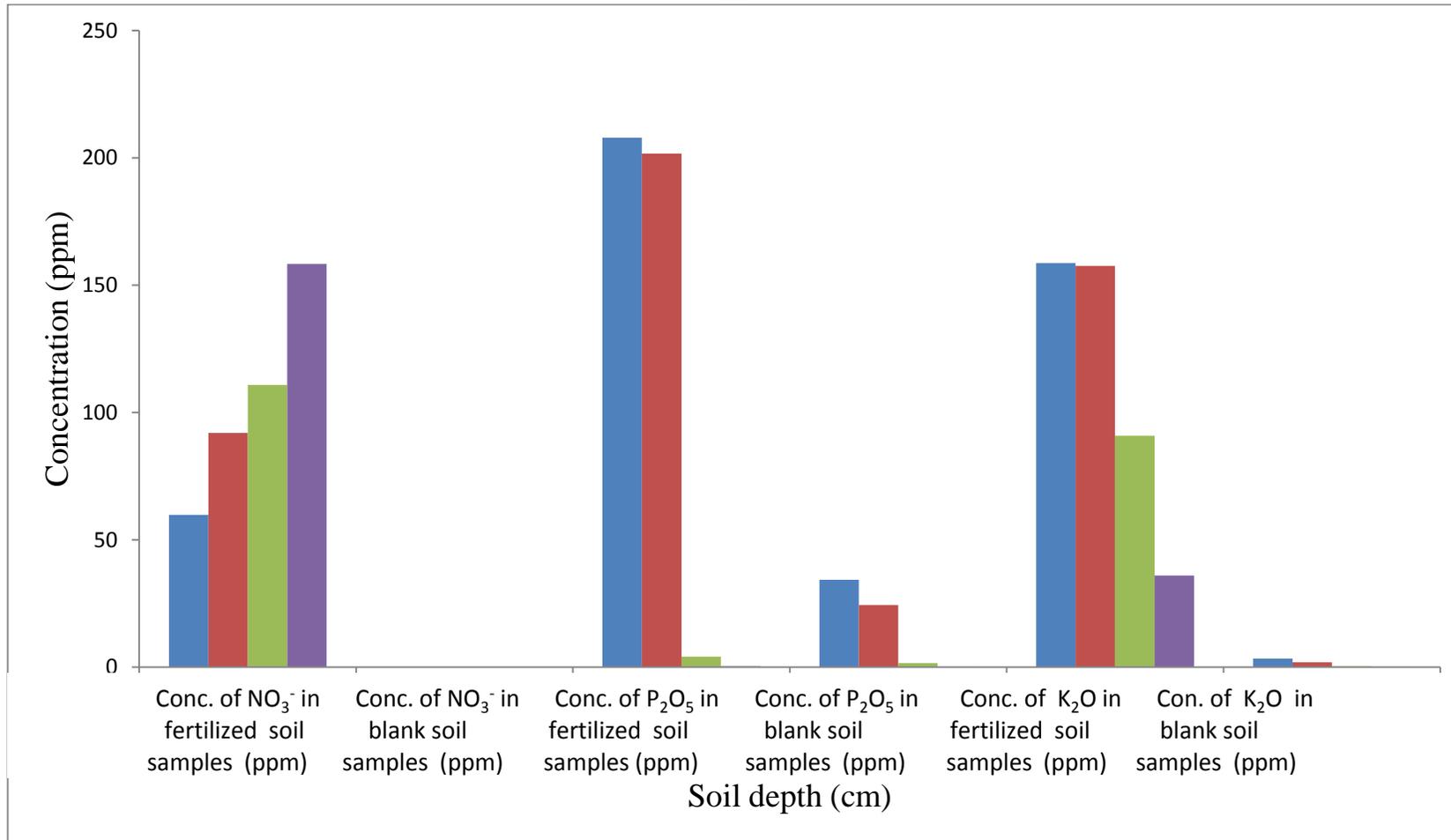


Figure (4.18.b): Histogram of comparison of the nutrients concentrations (NO₃⁻, P₂O₅ and K₂O) in blank and fertilized soil samples.

It is noted from the figures 4.18 (b) that there is an increase in the concentration of all nutrients (NO_3^- , P_2O_5 and K_2O) in samples of fertilized soil compared with the blank samples. This is due to the use of fertilizers which contain nutrients. The results show that with time the concentration of NO_3^- increases, while the concentration of P_2O_5 and K_2O decreases in the bottom layer of the soil, $\text{K}_2\text{O} > \text{P}_2\text{O}_5 > \text{NO}_3^-$, with means 110.8 ppm K_2O , 103.5 ppm P_2O_5 and 103.5 ppm NO_3^- . This means that K_2O is the most nutrient that accumulates on the soil compared to the other nutrients, followed by P_2O_5 , and finally NO_3^- .

The concentration of P_2O_5 and K_2O nutrients in samples of fertilized soil were found to be higher than the World Health Organization (WHO) acceptable maximum. P_2O_5 accumulation is the most on the surface of the soil because it makes complex compounds with organic matter, followed by K_2O , and finally NO_3^- .

4.4. Statistical Analysis:

The statistical analysis was conducted using IBM SPSS v24.0. Linear Regression test on all samples of leachate water, blank water, fertilized soil and blank soil, P- Value was calculated for heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}) and nutrients (NO_3^- , P_2O_5 and K_2O) in all samples. The results are shown in table 4.4 and table 4.5 respectively.

Table (4.4): P- Value for Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3} in leachate water samples and fertilized/ unfertilized soil samples.

Samples	Heavy metals	Zn^{+2}	Mn^{+2}	Cu^{+2}	Fe^{+3}
Leachate water samples	P- Value	0.001	0.003	0.006	0.002
Leachate blank water samples	P- Value	0.086	0.052	0.123	0.152
fertilized soil samples	P- Value	0.009	0.016	0.017	0.004
blank soil samples	P- Value	0.082	0.051	0.056	0.052

Table 4.4. shows that statistically the significant level (P- Value) for the selected heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}) in leachate water samples are < 0.05 , so there is significant variations in the concentrations of Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3} in leachate water samples because of the use of prolonged fertilizer. These heavy metals can leachate to the ground water and pollute it. On the contrary the significant level (P- Value) for the selected heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}) in leachate blank water samples are > 0.05 , so there is no significant variations of these heavy metals in sampling because the soil was unfertilized. Also statistically the significant level (P- Value) for the selected heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}) in fertilized soil samples are < 0.05 so there is significant accumulation of these metals due to prolonged fertilizer. furthermore the significant level (P- Value) for the selected heavy metals (Zn^{+2} , Mn^{+2} , Cu^{+2} and Fe^{+3}) in the blank soil samples are > 0.05 , so there is no variations of these heavy metals in the unfertilized soil.

Table (4.5): P- Value for NO_3^- , P_2O_5 and K_2O in leachate water samples and fertilized/ unfertilized soil samples.

Samples	Nutrients	NO_3^-	P_2O_5	K_2O
Leachate water samples	P- Value	0.015	0.002	0.006
Leachate blank water samples	P- Value	0.083	0.065	0.052
fertilized soil samples	P- Value	0.015	0.046	0.039
blank soil samples	P- Value	-	0.095	0.05

Table 4.5. shows that statistically the significant level (P- Value) for the selected nutrients (NO_3^- , P_2O_5 and K_2O) in leachate water samples are < 0.05 so there is significant variation in the concentrations of these nutrients in leachate water samples because of the use of prolonged fertilizer, these nutrients can leachate to the ground water and pollute it. On the contrary the significant level (P- Value) for the selected nutrients (NO_3^- , P_2O_5 and K_2O) in leachate blank water samples are > 0.05 , so there is no significant variations of these nutrients in sampling because the soil was unfertilized. Also statistically the significant level (P- Value) for the selected nutrients (NO_3^- , P_2O_5 and K_2O) in fertilized soil samples are < 0.05 so there is significant accumulation of these metals due to prolonged fertilizer. Furthermore the significant level (P- Value) for the selected nutrients (NO_3^- , P_2O_5 and K_2O) in blank soil samples are > 0.05 so there is no significant variations of these heavy metals in sampling because the soil was unfertilized.

Chapter Five
Conclusion and Recommendation

Conclusion and Recommendation:

1.5. Conclusions:

- The results which obtained from the present work show that the compound fertilizers 20/20/20, were used in Palestine contaminated the soil with heavy metals ions as Zn^{+2} , Fe^{+3} , Mn^{+2} and Cu^{+2} , nutrients as K_2O , P_2O_5 and NO_3^- .
- The study showed that the concentration of Cu^{+2} and Zn^{+2} in fertilized soil were obviously larger than that in the natural concentration world health organization (WHO).
- It was observed that the concentration of Fe^{+3} and Mn^{+2} in fertilized soil were obviously the same as the natural concentration world health organization (WHO).
- The concentration of heavy metals ions (Zn^{+2} , Fe^{+3} , and Mn^{+2}) in leachate water samples are larger than the natural concentration WHO. While the concentration of Cu^{+2} in leachate water samples is less than the natural concentration world health organization (WHO).
- The concentration of P_2O_5 and K_2O nutrients in samples of fertilized soil were found to be higher than the world health organization (WHO).
- NO_3^- is the most nutrients leached in the ground water than the other nutrients K_2O and P_2O_5 , it is may contaminate the ground water.

5.2. Recommendations:

To reduce the fertilizers environmental pollution, it is recommended to:

- Effective control of ministry of agricultural on the stores in which the chemical fertilizers are sold.
- Strict procedures should be taken on dealers selling chemical fertilizers that contain large amounts of heavy metals.
- The proper use of fertilizers in agriculture is essential to increase the productivity of the soil.
- Avoid the use of chemical fertilizers that contain large amounts of heavy metals.
- Farmers should be given awareness bulletins about the danger of chemical fertilizers and their negative impact on the elements of the environment. The production of new types of fertilizers to give the best production without polluting the environment.
- Scientists should do more analytical studies of the soil and plant tissue and groundwater.
- Farmers should hold a national campaign to restore agricultural waste and to recycle it in order to be used as an organic fertilizer.
- More training programs for agricultural engineers should be done.

Chapter Six

References

References

- Ajayi, S.O., Odesanya, B.O., Avwioroko, A.O., Adebambo B. G.S., Okafor,(March,2012). **Effects of long term fertilizer use on trace metal levels of soils in a farm settlement.** College of Pure and Applied Sciences, Caleb University, Imota. Lagos State; Chemistry Department, University of Ibadan, Oyo State; National Institute for Horticultural Research, Ibadan, Nigeria, pp. 44,46,47,50.
- Amundson Ronald, (1994). **Factors of soil formation.** University of California, Berkeley, pp.7.
- Andrew Sharpley, Mike Daniels, Karl VanDevender and Nathan Slaton, (1914). **Soil Phosphorus: Management and Recommendations,** University of Arkansas, pp. 16.
- Appel, C., Ma, L. Q., Rhue, R. D. and Reve, W., (2002), **Selectivities of potassium calcium and potassium-lead exchange in two Tropical Soils,** soil sci. soc. Am. J.,Vol. 67, pp.1707-1714.
- ATSDR, (2008). **Toxicological Profile for Manganese (Final).** U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA., pp. 539.
- Ayoub, A. S., McGaw, B. A., Shand, C. A. and Mid-wood, A. J., (2003). **Phyto availability of Cd and Zn in Soil Estimated by Stable isotope Exchange and Chemical Extraction.** Plant and Soil, Vol. 252, No. 2, pp. 291-300.

- Bang, J. and Hesterberg, D., (2004), **Dissolution of trace element contaminants from two coastal plain soils as affected by pH**, published in J. Environ. Qual., Vol.33, pp. 891-901.
- Baraghouthi Zaher, Amereih Sameer, Basel Natsheh and Mazen Salman, (2012). **Analysis of Macro and Micronutrients in soils from Palestine using Ion exchange Membrane Technonlogy**. University_ Kadoorie, Tulkarm, Palestine. pp. 1-6,46,47.
- Brian J. Alloway, (2008). **Zinc in Soils and Crop Nutrition**. Second edition, pp. 1,2,4,9,11-14, 18,19,46,49,50,95.
- Brady, N., and R. Weil, (2002). **The Nature and Properties of Soils**, 13th Edition. Prentice Hall. Upper Saddle River, New Jersey, pp. 960.
- Charles Hyland, Quirine Ketterings, Dale Dewing, Kristen Stockin, Karl Czymmek, and Greg Albrecht. Larry Geohring, (2005). **Phosphorus Basics – The Phosphorus Cycle.cornell university**, pp. 1,2
- Clark W. Gellings, and Kelly E. Parmenter, (2004). **Energy Efficiency in Fertilizer Production and use**, pp.1-3, 11,14.
- Diana Tracy and Brian Baker, (2003). **Heavy Metals in Fertilizers Used in Organic Production**, pp. 1,5.
- Dube, A., ZbytniewskiT, R., Kowalkowski, Cukrowska, E., and Buszewski, E., (2001). **Adsorption and Migration of Heavy Metals in Soil: Polish Journal of Environmental Studies**, Vol. 10, No. 1, pp. 1-10.
- Eun Hong, Quirine Ketterings, and Murray McBride, (2010). **Nutrient Management Spear Program** . Cornell University, pp. 1-2.

- Foth, H.D., and Turk, L.M. (1972). **Fundamentals of Soil Science**. 5th ed. John Wiley & Sons, New York, pp. 6.
- Gruhn Peter, Goletti Francesco, and Yudelman Montague, (2000). **Integrated Nutrient Management, Soil Fertility, and Sustainable Agriculture**, pp. 3,4.
- Halimah Ahmad Sai'd Staitai, Shehdeh Jodeh, and Marwan Haddad, (2012). **Fate of Amoxicillin, Ibuprofen, and Caffeine in Soil and Ground water Using Soil Columns**. An-Najah National University, Palestine, pp. 43.
- Henry D. Foth Boyd G. Ellis, (1988). **Fertility**. Michigan State University, pp.14, 40, 46,52, 62,74,79, 81, 110,141, 144, 160.
- IFA Statistics, (2007).
<http://www.fertilizer.org/ifa/Home-Page/STATISTICS>.
- Inaya Mizyed, Mohammed Al- SuBu and Marwan Haddad. June, (2000). **Impacts of Irrigation with high Heavy Metals concentration on soil and Ground Water**. An – Najah University, Nablus, Palestine, pp. 69.
- International Fertilizer Development Center, Alabama, and USA, May. (2001). **Fertilizer Feeds the World**, pp.1, 11.
- International Fertilizer Industry Association (IFA), (2001). **Fertilizer Indicators**. IFA, Paris, France, pp.17.
- Isam Jardaneh and Ahmad Bedare, (2010). **Soil Mechanics Laboratory Manual**. pp. 4-9, 17-19

- Joan, (1999). **Introduction to Environmental Chemistry. Physical and Chemical Properties of Soil. Davidson College.** pp.7
- Joan D. Willey, (1991). **Chemical Analysis of Soils**, pp. 1-17,35.
- Kabata – Pendias, A., Pendias, A., Pendias, , H, (2001): **Trace elements in soils and plants.** 3rd edition, CRC Press, USA, pp.331.
- Kadhum Shaimaa Taleb and Ayat Hussain. January, (2011). **A study of Changes in the Chemical Properties of Soil due to Irrigation by Ponuted River Water (Army Canal in Baghdad) for a long period,** pp. 3.
- Khwedim H. Kareem, Hussein Salah A., and Al- Adely J. A. (2010). **Heavy Metals in some soils of Baquba city: determination Distribution and Controlling Factors.** University of Diyala, pp. 166,167,173,175,177,181.
- Kotschi Johannes, (2013). A soiled reputation: **Adverse impacts of mineral fertilizers in tropical agriculture**, pp. 23, 35.
- Laing, G. D., Vanthuyne, D., Tack, F. M. G. and Verloo, M. G. (2007), **Factors affecting metal mobility and bioavailability in the superficial intertidal sediment layer of the Scheldt estuary**, Aquatic Ecosystem Health & Management, Volume 10, Issue 1 , pp. 33 – 40.
- Matson PA, Naylor R, and Ortiz-Monasterio I.(1998). **Integration of environmental, agronomic, and economic aspects of fertilizer management.** Science 280, pp.112–115.
- McBRIDE, M.B, (1994). **Environmental Chemistry of Soils.** 1st Edition; Oxford University Press, pp. 416.

- McCauley Ann, Jones Clain, and Jacobsen Jeff, (2005). **Soil and water management**, pp. 2.
- McKenzie Ross H. PhD, P. Ag., January (2013). **Potassium Fertilizer Application in Crop Production**, pp. 1-7.
- Michael Pidwirny, (2006). Fundamental of Physical Geography, 2nd Edition " Chapter 10: **Introduction to The Lithosphere : Introduction to Soil**. University of British Columbia Okanagon, pp. 32
- Mohammed Azeroual. January, (2012). Environmental and soil chemistry, pp. 7.
- Mohammed M. AL-SUBU, Marwan Haddad, Numan Mizyed and Inaya Mizyed. September, (2002). Impacts of Irrigation with water containing Heavy Metals on Soil and Groundwater – Asimulation Study. An – Najah University, Nablus, Palestine, pp. 142.
- Omama Monther Refa'I, Marwan Haddad and Maather Sawallha. (2015). **Assessing the Transport of Heavy Metals from Al-Faria Main stream into Soil and Groundwater**. An – Najah University, Nablus, Palestine, pp. 23.
- Osama Zaki Mohammed Naser, Shehdeh Jodeh and Marwan Haddad, (2011). **Kinetics Of Groundwater Nitrate (NO₃⁻¹) In Soil Leachate In Tulkarem City Using Soil Columns**. An – Najah University, Nablus, Palestine, pp. 7,10,11,14,15,24,25,29,97.
- Palestinian Central Bureau of Statistics, (05/06/2012). **Press Release on World Environment Day**, pp.1.

- Perk, M. V. D.(2007). **Soil and Water Contamination from molecular to catchmentscale**, Tylor & Francis Group, pp. 389.
- Raven JA, and Taylor R. (2003). **Macroalgal growth in nutrient enriche destuaries: a biogeochemical perspective. Water, Air and Soil Pollution: Focus 3**, pp.7–26.
- Raymond A.Wuana1 and Felix E. Okieimen. **HeavyMetals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. August 2011**, pp. 1,2,5,6,16
- Rehm George and Schmitt Michael, (1997). **Potassium For Crop Production**. Minnesota Extension Service. University Of Minnesota. College of Agricultural, Food, And Environmental Sciences, pp. 1-6.
- Roberts, T.L., (2009), **The Role of Fertilizer in Growing the World’s Food: Better Crops**, Vol. 93, No. 2, pp. 12,15,40.
- Ross H. McKenzie PhD, P. Ag., January (2013). **Potassium Fertilizer Application in Crop Production**, pp. 1-7
- Schulte, E. E., and Kelling, K.A., (1914). **Soil and Applied Manganese**, pp. 1-2.
- Schulte, E. E., and Kelling, K.A., (1914). **Soil and Applied Potassium**, pp. 1-2.
- Schulte, E. E., and Kelling, K.A., (1996). **Soil and Applied Phosphorus**, pp. 1-2.
- Schulte, E. E., and Kelling, K.A., (2004). **Soil and Applied Copper**, pp. 1-2.

- Schulte, E. E., and Kelling, K.A., (2004). **Soil and Applied Zinc**. pp, 1-2.
- Shacklette, H.T., and J.G. Boerngen, (1984). **Element concentrations in soils and other surficial materials of the coterminous United States**. USGS Paper 1270. Washington, DC: US Govern. Printing Office, p. 6.
- Siegel, A., and Siegel, H, (2000). **Metal Ions in Biological Systems: Manganese and its role in biological processes**.Vol. 37, CRC Press, pp. 816.
- Silveira. M. L., Alleoni, L. R. and Guilherme, L. R. G. (2003), **Biosolids and Heavy Metals in soils**, Sci. Agric. (Piracicaba Braz.), Vol. 60, No-4, pp. 32.
- Smith, Bt R. S., Dbturk, Bt R. S., Bauer, F. C. and Smith, L. H. (1928). **Agricultural Experiment Station**. Soil Repoet NO. 40. White Side Country Soils. University of Illinois, pp.7, 14-30.
- Syers, J.K., Johnston. A.E., and Curtin, D. (2008). **Efficiency of soil and fertilizer phosphorus use: Reconciling changing concepts of soil phosphorus behaviour with agronomic information**, pp. 1,2,53.
- Tomoyuki Makino, Yongming LUO, Longhua WU, Yasuhiro SAKURAI1, Yuji MAEJIMA, Ikuko AKAHANE and Tomohito ARAO, (2010). **Heavy Metal Pollution of Soil and Risk Alleviation Methods Based on Soil Chemistry**, pp. 38, 39.
- United States Department of Agriculture, (2000), **Heavy Metal Soil Contamination**, September, pp.1.

- U. S. Environmental Protection Agency, November (2003). **Ecological Soil Screening Level For Iron. Office of Solid Waste and Emergency Response 1200 Pennsylvania Avenue, N.W. Washington, DC 20460, pp. 5,7,12,13,17,35.**
- Walworth James. January, (2013). **Nitrogen in Soil and the Environment.** The university of Arizona, pp. 1-3.
- Wolman, M. G., and Fournier, F. G. A., (1987). **Land Transformation in Agriculture Edited.** SCOPE. Published by John Wiley & Sons Ltd, pp. 304, 305.
- Wuana¹ Raymond A. and Okieimen Felix E.. August (2011). **Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation,** pp. 1,2,5,6,16.

- أحمد عزيز الدين أبو بكر عبد الحافظ. الأثر البيئي للتسميد المعدني المتعاقب على بعض خواص التربة والنباتات النامية عليها، 2008، صفحة 3.
- د.محمد بن عبد الرحمن، د.محمد محمد الجرواني، د. علي فتحي حمائل.دراسة تأثير التسميد بالأسمدة الفوسفاتية على تراكم عنصر الكاديوم في التربة وفي الأجزاء النباتية لبعض محاصيل الخضر.التقرير الفني النهائي للمشروع، 2010م، رقم 2021.كلية العلوم، صفحة 19.
- غفران فاروق جمعة، رياض حسن الأنباري، تقييم التلوث بالعناصر الثقيلة في الأراضي الزراعية الواقعة في منطقة جسر ديالي، 2010م، صفحة 105،108،111.

جامعة النجاح الوطنية
كلية الدراسات العليا

دراسة حركة المعادن الثقيلة والمغذيات الناتجة عن استخدام الأسمدة باستخدام أعمدة التربة البلاستيكية

إعداد

سارة محمد أحمد حسن

إشراف

د. أحمد أبو عبيد

د. شحدة جودة

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في العلوم البيئية بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2016

ب

دراسة حركة المعادن الثقيلة والمغذيات الناتجة عن استخدام الأسمدة في نوع واحد من التربة في فلسطين باستخدام الأعمدة البلاستيكية

إعداد

سارة محمد أحمد حسن

إشراف

د. أحمد أبو عبيد

د. شحدة جودة

الملخص

حيث أنه لا يوجد أيّ بيانات حول محتوى العناصر الثقيلة في الأسمدة المستخدمة في فلسطين، هذه الدراسة تزود ببيانات جديدة يمكن استخدامها من قبل وزارة الزراعة في فلسطين، قياس تركيز العناصر في الأسمدة يظهر معلومات أكثر عن معدل هذه العناصر في الأسمدة.

في هذه الدراسة تمّ تحديد تركيزالعناصر الثقيلة الآتية: الزنك والمنغنيز والحديد والنحاس التي ترشح من الأسمدة على التربة باستخدام جهاز الامتصاص الذري اللهبّي flame atomic absorption spectrophotometer (AAS)

بالإضافة إلى تحديد تركيز بعض المغذيات التي ترشح من التربة: الفسفور والبوتاسيوم والنيتروجين باستخدام جهاز الامتصاص الطيفي للأشعة فوق البنفسجية والضوء المرئي Ultraviolet visible (UV-VIS) والنيتروجين في عينات الماء باستخدام جهاز Photometer Nitrate.

وذلك في نوع واحد من التربة الحمراء الموجودة في مدينة نابلس ونوع واحد من السماد وهو السماد المركب الذي يحتوي على عناصر البوتاسيوم والنيتروجين والفسفور بنسبة 20/20/20 والمستخدم في فلسطين.

الرسومات البيانية المختلفة استخدمت لتوضيح النتائج.

أظهرت النتائج أنّ السماد المركب 20/20/20 المستخدم في فلسطين هو مصدر رئيسي لعدة عناصر ثقيلة ملوثة ومغذيات، كما أظهرت النتائج الاحصائية أنه يوجد تغير هام في تركيز العناصر الثقيلة والمغذيات في عينات التربة المسمدة وعينات الماء الراشح عنها لهذا فإن هذه العناصر مثل الخارصين والنحاس والحديد والمنغنيز بالإضافة إلى بعض المغذيات مثل الفسفور

ج

والبوتاسيوم تعمل على تلويث البيئة بتراكمها على سطح التربة، ورشوحها إلى المياه الجوفية وتلويثها مثل النيتروجين والخاصين والحديد والمنغنيز.
تشير هذه البيانات إلى أن التربة المسمدة بالسماذ المركب 20/20/20 غنية بعناصر ثقيلة سامة خاصة الخاصين، وبعض المغذيات خاصة النيتروجين الذي يسبب تلوث المياه الجوفية.