An-Najah National University

Faculty of Graduate Studies

Assessing the Transport of Heavy Metals from Al-Faria Main Stream into Soil and Groundwater

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Dedication

Every challenging work needs self efforts as well as guidance of elders especially those who were very close to our heart. I dedicated my humble effort to my sweet and loving parents Monther and Sameera Refa'i, whose affection, Love, encouragement and prays of day and night make me able to get such success and honor. To my beloved Hamdi who has always been my nearest thank you for your unconditional love and supports with my studies, I am honored to have you as my husband. To my brothers (Bara', Rayan and Abdullah), my sisters (Ata' and Hiba) and my Aunts (Maha and Mayzoon), thanks for your moral support and being in my side step by step. It is also dedicated to all my friends, their friendship is so special to me, they always have a shoulder to lean on through the good and bad times, thank you for being the true friends you are. Finally I dedicated my effort to my little Teema, you changed my life and made me a mother, this feeling gave me the strength to go ahead and get this achievement. I hope you are proud of your mother!

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Assessing the Transport of Heavy Metals from Al-Faria Main Stream into Soil and Groundwater

أقربأن ما اشتملت عليه هذه الرسالة إنما هي انتاج جهدي الخاص, باستثناء ماتم الإشارة إليه حيثما ورد, وأن هذه الرسالة ككل, أوأي جزء منها لم يقدم لنيل أي درجة أولقب علمي أو بحثي لدى أية مؤسسة تعليمية أوبحثية 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: أمامة منذر الرفاعي**

Signature **التوقيع:**

Date **التاريخ: 2015/12/17**

Table of Content

List of Tables

List of Figures

List of Annexes

Assessment of Heavy Metals Transport From Wadi Al-Faria Stream into Soil and Groundwater

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Abstract

Faria catchment is one of the most important region in the West Bank, Palestine, due to the intensive agricultural activities and it contains a lot of groundwater wells and springs which used in irrigation and domestic consumption. Therefore, the quality of this water resource is an important issue. Heavy metals are one of the most toxic pollutants that must be taken in consideation, so the aim of this research is to assess the concentrations of Nickel, Cadmium, Copper and Chromium in wadi AlFaria stream, soil and groundwater in six selected Faria locations. Then comparing them with permissible limits of heavy metals in irrigation water and soil. A second objective of this research is modeling the transport of heavy metals in soil using column study. In this experiment the columns used were defined as follow: two columns represent the concentration of heavy metals for 5years, the other two columns for 10years and the last two columns for 20 years.Thereafter, to know the fate of selected heavy metals in soil and if there is possibility to reach and pollute groundwater in Faria catchment.

Results show that Ni, Cd, Cu and Cr are found in wadi AlFaria stream, soil and groundwater wells in the six selected locations at very low concentrations which are under the permissible limits. Also the concentrations in dry season are larger than it in wet season. The

concentrations of Ni, Cd, Cu and Cr in stream, soil and groundwater wells at dry and wet seasons for the six selected locations were subjected to analysis of variance (ANOVA). A probability ≤ 0.05 was considered as significant. ANOVA showed that there is no significant variation in the concentrations of Ni, Cd, Cu and Cr with sampling location in dry and wet season.

According to column leaching experiment, the results showed that the concentrations in the effluents were too small and decreased with time through the experiment period which was 24 hours. And at the long term of time as appeared in the columns of 20yr-concentration the relation tends to be linear. Most of Ni, Cu, Cd and Cr are accumulated in the top and middle layers of the columns. According to R^2 values the concentration-depth relation is linear, when depth increases, the concentration decreases. That means the soil is homogeneous and heavy metals adsorption occurs.

The average depth in soil at which the concentrations of selected heavy metals becomes zero in the columns of 5yr-concentartion, 10yr-concentration and 20yr-concentrations are 32.97cm, 48.10cm and 38.50cm respectively.

In general, Faria soil has a high adsorption capacity for the selected heavy metals at different high inflow concentrations. But the presence of heavy metals in groundwater samples means they were transported from the stream, adsorbed by soil and reach the groundwater even at low concentrations, which indicates a potential risk for pollution at the long term of time.

Chapter One

General Introduction

Chapter One

General Introduction

1.1 Importance

Faria catchment has intensive agricultural activities, so it is considered as one of the most important region in the West Bank, Palestine. It is figured that the only water resource for the irrigation and domestic uses in the catchment is the groundwater wells and springs. The untreated wastewater from the eastern part of Nablus city and also from Al- Faria refugee camp threats the groundwater quality in Faria catchement, since they are discharging into Faria wadis containing pollutants, some are biodegradable and others are very toxic like heavy metals. The polluted water infiltrates to a large extent into shallow and deep groundwater bodies. (Shadeed et al, 2011).

In addition, most of the agricultural and domestic wells in the catchment were drilled in the vicinity of the main wadi, so this enhances the probability of heavy metals in the stream to reach groundwater through the soil.

1.2 Background

Although the world as a whole may possibly has enough water to supply population, water resources on the surface of earthare not equally spread worldwide. In semi-arid regionsthere is no enough water to sustain domestic and irrigation demands. Since water scarcity is almost endemic problem, groundwater is the main water resource foragriculture and household uses in semi-arid regions. (Mvungi et al., 2005 and UN, 2006).

Unfortunately, groundwater is liable to pollution. The use of fertilizers and pesticides in agricultural areas, gas stations, electronics manufacture, fuel oil, municipal sewer lines and landfills and other man-made products, all these are sources of potential groundwater contamination. When pollutants can move through the soil and end up in the groundwater, it becomes unsafe and unfits for human use.(EPA, 1991).

Groundwater contamination causes irretrievable damage to organisms and spreads epidemic and chronic diseases. Heavy metals are one of the most toxic pollutants, since high concentrations of these metals can cause deleterious side effects, such as inhibition of enzymes, genetic damage and hypertension etc. Industrial activities are one of the main sources of heavy metals that may find their way to water bodies. (Fazila et al.,2012).

Industrial and consumer waste, or even acidic rain that break down soil, are ways for heavy metals to enter water supply such as streams, lakes, rivers, soil and groundwater. (Lenntech, 1998).

1.3 Problem Statement

The groundwater in Faria catchment is the main water resource for domestic and agricultural uses, so the quality of groundwater is a wide important issue. Heavy metals in wadi Faria stream could threat the quality of groundwater in the catchment, if there was a probability of transportation through soil and contaminate groundwater bodies. This kind of pollution could affect the health of the general population in the catchment.

1.4 Research Statement

This research will help to assess heavy metals transportation from wadi Al-Faia stream through soil into groundwater and to find the potential accumulation in a long term of time. That would be of great importance due to the adverse effect of heavy metals on soil, plant, animals and human health, in order to take the best decisions and practices that protect the groundwater in the catchment from this kind of pollutants.

1.5 Research Objectives

The mains objectives of this research are:

1- To assess heavy metal concentrations including: Cr, Ni, Cu and Cd and to construct their profile in stream, soil and groundwater in selected Faria locations.

2- Modeling the transport of heavy metals in soil using column study.

Chapter Two

Study Area

Chapter Two

Study Area

2.1 Geography

Faria catchment is located in the northeastern part of the West Bank, Palestine and extends from the ridges of Nablus Mountains down the eastern slopes to the Jordan River. The catchment is funnel shaped with an area of 320 km^2 which accounts for about 6% of the total area of the West Bank. The Faria catchment lies within the Eastern Aquifer Basin, which is one of the three major groundwater aquifers forming the West Bank groundwater resources and it is overlies three districts of the West Bank, these are: Nablus, Tubas and Jericho.(Shadeed, 2008) **Figure 2.1** Shows the regional location of Faria catchment.

The borders of the catchment are: North Jordan and Fassayel-Auja drainage basins from the north and south respectively, Alexander, Yarkon and Al-Khidera drainage basins from the west and Jordan River from the east. The western boundary of the study area lies at the main catchment between the Mediterranean Sea and the Jordan River. (Shadeed, 2005)

2.2 Topography and Geology

Faria catchment is confined by two ridges extending in the Northeast/ Southwest from Nablus city to the Jordan River. It is notable that the topography of the region changes from about 900m above mean sea level in the Western edge of the catchment near Nablus to about

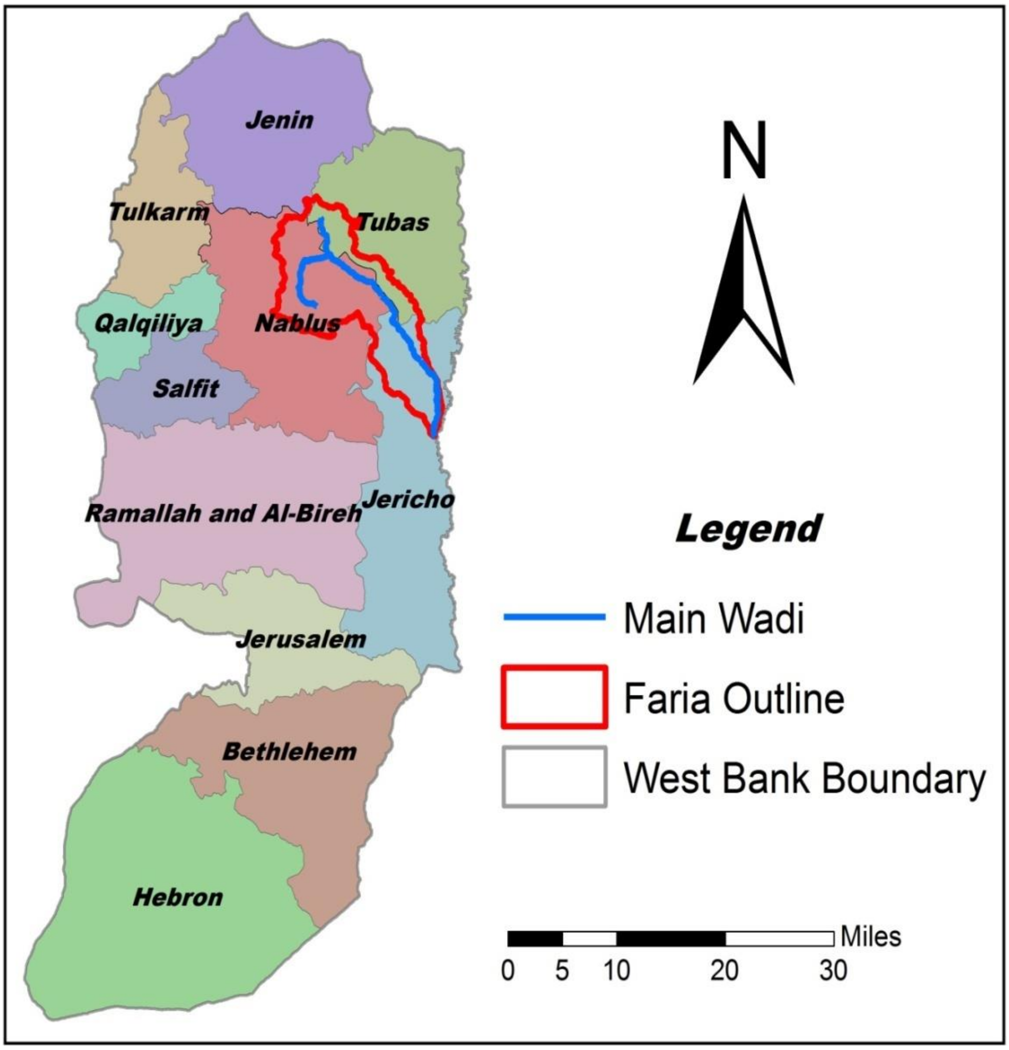


Figure 2.1: Regional Location Map of Faria Catchment.

250m below sea level in the east at the confluence with the Jordan River. This means that in about 30km of length there is a 1.3km drop in elevation which indicates an average slope of more than 4%. (EQA, 2004).

Geologically, the Faria catchment is part of the larger regional Dead Sea Rift Zone which has formed a number of horsts and grabens which confine the drainage of Faria catchment surface water system. Faria catchment is a structurally complex system with the Faria Anticline that trends northeast to southwest acting as the primary controlling feature. Additionally, a series of smaller faults and joints perpendicular to this anticline have a significant effect on the surface water drainage area. (Shadeed, 2008).

Many sedimentary formations can be found in Faria catchment. The most common formation in the northern part of the catchment is of Albian-Cenomanian age and consists of dolomite, limestone, and marl. Alluvium of Quaternary age is found as the surface exposure around the village of Tubas. In the central part of the study area, the most common formations are of Cenomonian age and consist of limestone, dolomite, marl, chalk and chert. The southern part of the study area has a dominant exposure of limestone, marl and dolomite of Turonian age (Birzeit University and Calvin College, 2003).

2.3 Climatology

Wadi Faria catchment is dominantly a Mediterranean, semi-arid climate, characterized by mild rainy winters that last about six months and moderately dry and hot summers. The winter rainy season is from October to April in the upper zone, while in the central and lower zones, rainfall events usually occur between November and April. The annual average precipitation ranges between 150 and 660 mm in the catchment. While in summer the hottest months are July and August when average maximum temperatures can reach up to 40 ^{o}C. **Figure 2.2** presents the spatial presentation of the rainfall data within the Faria catchment.. the relative humidity is low in Faria catchment especially in summer months because the watershed is located on the eastern side of the West Bank mountains. The source of humidity in the region is the Mediterranean Sea and only western winds bring humidity to the area. (EQA, 2004)

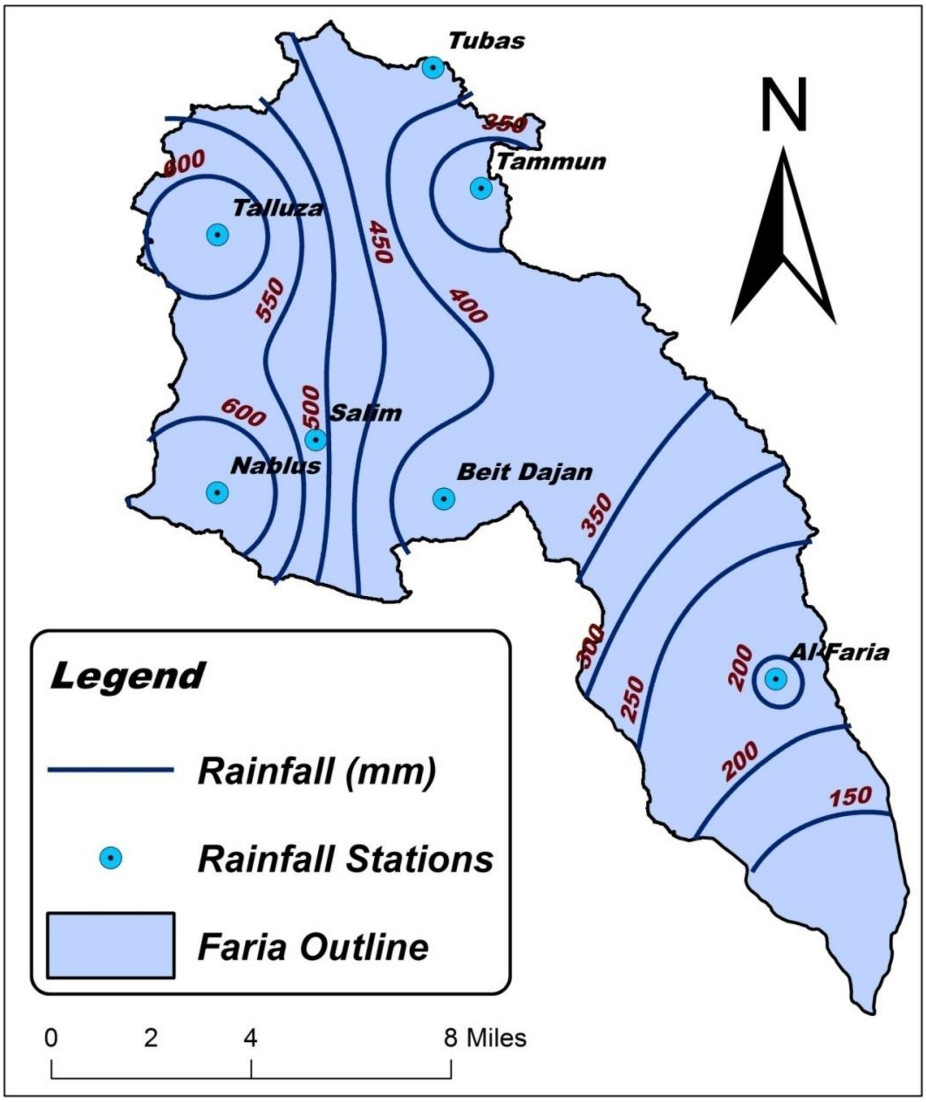


Figure 2.2: Rainfall Stations and Rainfall Distribution within the Faria Catchment.

2.4Soil and Land Use

2.4.1 Soil

There are six soil types found in the Faria catchment. These are; Regosols, Grumusols, Loessial Seozems, Brown Rendzianas and Pale Rendzinas, Brown Litholsols and Loessial Arid Brown Soils and Terra Rossas, Brown

Rendzianas and Pale Rendzinas.Two basic soils cover most of the Faria catchment. These two types are Terra rossas and Brown rendzinas/pale rendzinas, taking up more than 65% of the total area. The total area of this type of soil is 131.1 km^2. This type of soil is common in the highland parts of the catchment. The parent materials for this type of soil originated from mainly dolomite and limestone. Soil depth varies from 0.5 to 2 meters depending on the slope of the soil. The texture of these soils is clay to clay loam. (EQA, 2004)

According to the soil type; it has been shown that 33% of the northeastern part of west Bank has a high vulnerability to groundwater contamination, and that is important to consider since Faria catchment located in this part. (Ataallah, 2010)

2.4.2 Land Use

Faria catchment is one of the most important agricultural areas in the West Bank. The agricultural land in the catchment is composed of an arable land and heterogeneous agricultural areas. The area of the agricultural part of Faria catchment is 115,447 dunum which represents about 34.4%. The artificial surfaces in the catchment are composed of refugee camps, urban fabrics, Israeli colonies and military camps. The total area of the artificial surfaces is 18,047 dunum presenting about 5.5 % of the total area of the catchment. The forests and semi natural bodies in the Faria catchment occupy an area of about 20,1087 dunum representing 60% from the total area. (Shadeed, 2005 and EQA, 2004) **Figure 2.3** represents the land use map of the Faria catchment.

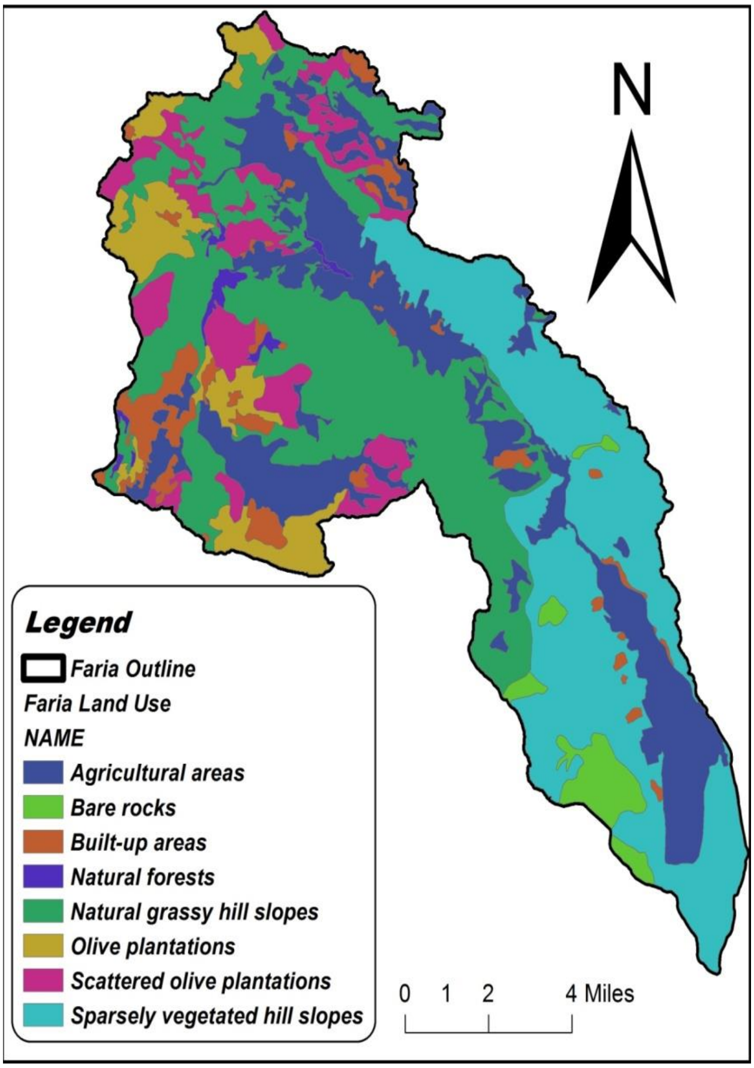


Figure 2.3: Land Use Map of the Faria Catchment.

2.5 Water Resources and Quantity

In the Faria catchment, water resources are either surface or groundwater. Water resources are replenished from rainfall. In the winter, the majority of generated surface runoff leaves the catchment, as there is no infrastructure to store excess water. Groundwater aquifers are usually utilized through springs and wells. Most of the springs are located in the upper and middle parts of the catchment. Within the Faria catchment there exists 13 fresh water springs that are divided into four groups. These groups are Faria, Badan, Miska and Nablus. Annual discharge from these springs varies from 3.8 to 38.3 MCM/year with an average amount of 14.4 MCM/year. There are 69 wells in the Faria catchment; of which 61 are agricultural wells, 3 are domestic and 5 are Israeli wells. **Figure 2.4** represents the distribution of the wells and springs along the main wadi in the Faria catchment. All these wells are located in the study area mainly in the areas of Ras Al-Faria, Al-Aqrabanieh, Al-Nasaria, Froush Beit Dajan and Jiftlik along the flexure of wadi Faria. The total utilization of the Palestinian wells ranges from 4.4 to 11.5 MCM/year. (Shadeed, 2005).

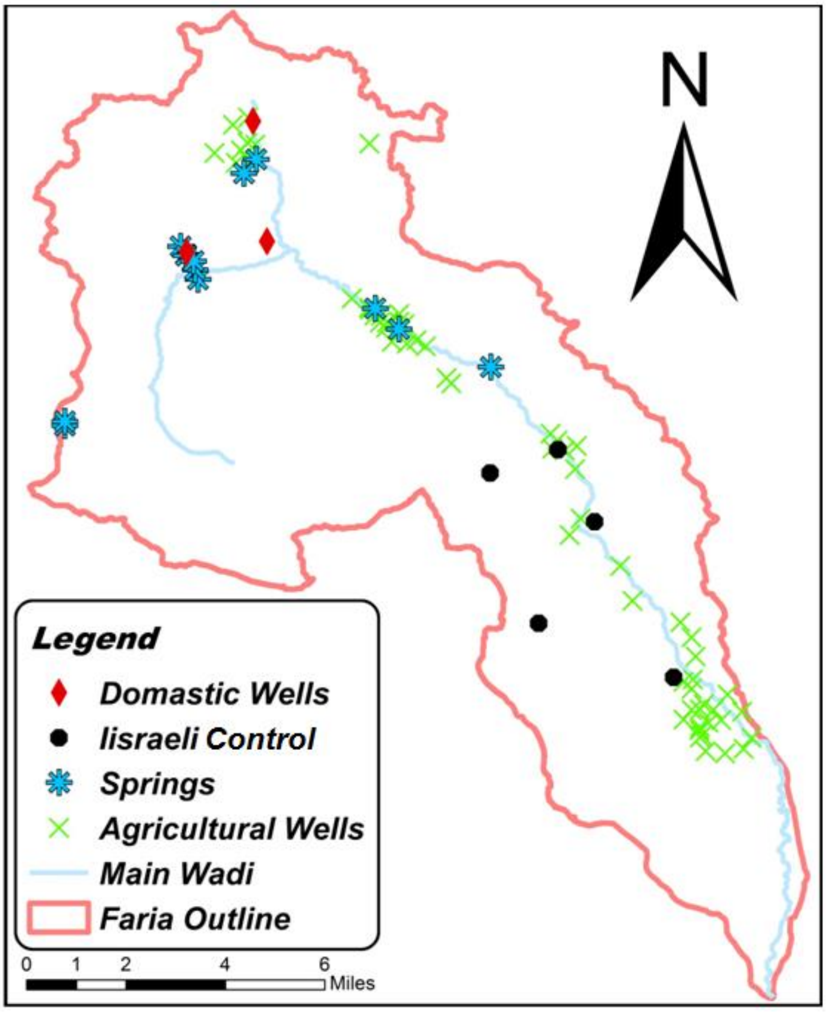


Figure 2.4: Distribution of Wells and Springs in Faira Catchment

2.6 Water Quality

In wadi Al-Faria stream DO changed due to aeration in natural stream from 0.55 mg/l upstream to DO level of 5.1 at the downstream, average TKN changed from 233 mg/l at upstream to about 160mg/l at the downstream, average TDS reduced from 2000 mg/l to 500 mg/l at downstream, and TSS also reduced from average 1604 at upstream to about 266 mg/l at downstream. (Alawneh, 2013). Also there is an increase in the concentrations of some heavy metals and organic compound in the Faria stream as follow: 1.69 mg/L Ni, 0.2 mg/L Cr, 1.2 mg/L Cu and 0.03 ppb CH_3Br. (Duraidi, 2014).

The quality of spring water in Al-Fara'a area is considered fair in terms of chemical quality of water. The water in the most springs in Faria catchment has low concentration of total dissolved solids and nitrate ion for most spring discharge points. The quality of water may be considered suitable for all purposes of water use including domestic. In some occasions the concentration of nitrate exceeded the internationally allowable limit of 50 mg/l. (EQA, 2004)

In Faria catchment, there is an accumulation of heavy metals in soil profile such as arsenic, lead and cadmium; also there is an increase in the concentrations of Ni, Cu and Cr in wadi Al-Faria stream. (Mohammed Abu Baker, 2007)

Potential future risk of some heavy metals and organic compound of Faria stream was estimated using chemical risk formulas. The results indicated that there is a great potential of non-carcinogen toxicity if these pollutants have been proven to reach the drinking water resources. Quality analysis which was made for the groundwater samples from a well that is located next to the main stream showed that there is microbial and chemical pollution in the well. And that evidence of wadi-aquifer interaction in the area. (Abboushi, 2013and Abu Hijleh, 2014)

Surface runoff in the Faria catchment is considered high compared to other catchments in the West Bank. Within the catchment the runoff decreases from west to east with decreasing rainfall. The city of Nablus discharges untreated industrial and domestic wastewater effluents to Al-Badan wadi while Al-Faria Refugee camp discharges untreated domestic wastewater to Al-Faria wadi.

Therefore, the wadi flow of the Faria catchment is a mix of:

1. Runoff generated from rain. This includes urban runoff from the eastern side of Nablus City and other built up areas in the catchment.
2. Untreated wastewater of the eastern part of Nablus City and of Al-Faria Refugee camp.
3. Fresh water from springs which provide the base flow for the catchment main wadi preventing it from drying up during hot summer. (Shadeed, et al., 2011).

In addition, Wadi Faria is an important agricultural area which is considered as a basket food that provides the West Bank, Palestine with the main agricultural products. So there are using of fertilizers and pesticides for the different types of crops. (Shadeed, et al., 2006)

As a result, the Discharge of untreated industrial wastewater and unbalanced use of fertilizers and pesticides that contain heavy metals cause pollution of the scarce water resources, both surface water as well as groundwater in Wadi Al-Faria catchment. (Jarrar, et al., 2005).

Chapter Three

Literature Review

Chapter Three

Literature Review

3.1 Heavy Metals

Regardless of metal's atomic mass or density, any toxic one which has metallic properties can be called heavy metal. They include the transition metals such as Copper, Lead, and Zinc, Actinides, Lanthanides, and some Metalloids. Leaded petrol, industrial effluents, and leaching of metal ions from the soil into lakes and groundwater by acid rain, all these are sources of heavy metals that cause environmental pollution. (Singh, 2007 and Daintith, 2000)

Heavy metals are found naturally in the earth crust, but indistinctive human activities have drastically affected their geochemical cycles and biochemical balance. This lead metals to accumulate in plant parts having secondary metabolites, which is responsible for a particular pharmacological activity. Long term exposure to heavy metals such as Cadmium, Copper, Lead, Nickel, and Zinc can cause deleterious health effects to human. (Singh et al., 2011).

Contaminant metal (or metalloid) are species that exist in high concentration or occurs where it is unwanted, and cause a detrimental human or environmental effect. Common contaminant metals/metalloids include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper

(Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants including aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U). (Mcintyre, 2003).

Table 3.1: The Atomic mass for Cd, Cu, Cr and Ni and their potential health effects under long-term exposure. (EPA, 2009)

Heavy Metals	Atomic mass	Potential Health Effects from Long-Term Exposure Above the MCL
Cd	112.41	kidney damage
Cu	29.00	Liver or kidney damage
Cr	24.00	Allergic dermatitis
Ni	58.69	Decreased body weight; heart and liver damage; dermatitis.

3.2 Anthropogenic Sources of Heavy Metals

Heavy metals are used in a large variety of industrial products. Their release into the environment occur at the beginning of the production chain, whenever ores are mined, during the use of products containing them, and also at the end of the production chain. Parent rocks and metallic minerals are the natural sources, while agricultural and industrial activities are the main anthropogenic sources. The agricultural activities include the use of fertilizers, animal manures and pesticides. On balance, the industrial including metallurgical activities, mining, metal finishing and others like energy production and transportation, microelectronic products and finally waste disposal. Heavy metals can be released into the environment in gaseous, particulate, aqueous or solid form and emanate from both diffuse or point source. (Bradl, 2005)

Rapid population growth around the world requires intensive land use for the production of food, which implicate repeated and heavy input of fertilizers, pesticides, and soil amendments which contain many heavy metals that introduced into soils and also can influence groundwater and surface water bodies by infiltration, since soil surface and groundwater are closely interconnected system. (Probstein, 1994 and Voss, et al., 2001).

Some kinds of fertilizers like phosphatic one contains amounts of Cd, Zn and other heavy metals depending on the parent rock that fertilizers has been produced from. On the other hand, pesticides application lead to increase the accumulation of heavy metals, especially Hg from methyl mercurial, As and Pb from lead arsenate into soils and groundwater. (Mackay, Cherry, 1989 and Teutsch, et al.,1996)

Manufacturing of Ferro-alloys (special steel), arc-welding, Ni/Cd batteries, water pipes, pigments, anti-corrosive metal coatings, good conductor of heat and electricity, wood treatment, surgical and dental prostheses, molds for ceramic and glass containers, computer component and catalystsm, passivation of corrosion of cooling circuits and others are some industrial activities enhance the accumulation of heavy metals like Nickel (Ni), Cadmium (Cd), Copper (Cu) and Chromium (Cr) in environment. (Bradl, 2005).

3.3 The Mobility of Heavy Metals in Soil

The industrial activities have a very negative impact on the environment, due to the accumulation of metallurgical waste. Dust and metals can migrate to surface water and transport into soil and groundwater. The degree of mobility in the soil fractions varies from metal to another depending on the physical, chemical and biological processes and interactions between them. Bioavailability of heavy metals depends on several soil properties, which are include: granulometric composition, organic matter content, occurrence and form of cations, pH value, sorption capacity, content of macro and micronutrients, oxidation-reduction potential, activity of microorganisms, and, resistance of the soil. (Fijalkowski et al., 2012)

According to the granulometric composition of soil, it is observable that when the grain size decrease, the heavy metal content of the soils increase, since sandy soils consisting of coarser grains and possessing small adsorbing capacity has the lowest heavy metal concentration while The highest metal concentration was determined in silty loam consisting of the finest grains. (Szabo and Czeller, 2009)

Soil pH influences the solubility of heavy metals in soil. It has been shown that the decrease of the soil pH causes effective metals mobilization. (Ma and Dong, 2004) Besides pH, the quality of organic matter plays a very important role in mobility, availability and complexity of heavy metals. Increasing the amount of organic matter in the soil, helps to minimize the absorption of heavy metals by plants. Soil rich in organic matter actively retains metallic elements. (Barančíková and Makovníková, 2003)

All soils with high sorption capacity for cations, (i.e. containing a large amount of clay minerals), have the ability to accumulate metallic elements and the forms at which heavy metals occur in soils significantly affected their mobility. Cd, Zn and Mo are the most mobile elements, while Cr, Ni and Pb are the less mobile ones. (Fijalkowski et al., 2012)

Soil redox potential can influence the solubility of heavy metals. In conditions where oxidation reactions are involved, the solubility of heavy metals increases with decreasing pH. But in reducing conditions, the solubility of Zn, Cu, Cd, and Pb is higher in alkaline pHs. (Silveira, et. al, 2003)

The lower the amount of micronutrients in the soil, the higher accumulation of several heavy metals in plants are. Microorganism activity in ryzosphere is also a major determinant of growth of the plant and its resistance to pathogens. Soil contamination processes are constant, but compared to other elements of the environment, they are the most capable to defend themselves, acting as a buffer for pollutants. Resistance to contamination, regarding the pressure of degrading factors, land owes to its physical, chemical and biological properties. Resistance of soil is biochemical, because it results from the ability of plants to absorb and neutralize chemically active pollutants. (Fijalkowski et al., 2012)

3.4 Surface Water and Groundwater Interaction

The untreated wastewater from agricultural sources and atmospheric deposition are discharged directly into streams by surface runoff or rainwater containing heavy metals, this leads to potential health and environmental risks for people living in downstream areas (Smail et al., 2012).

Due to rapid industrialization and urbanization, and intense agricultural activities in most countries of the world, groundwater and surface water in agricultural areas are having a serious risk of metal pollution. (Klavins et al., 2000; Li and Zhang, 2010).

Trace metals could infiltrate to deeper soil layers, and eventually reach groundwater (Bichet et al., 2013). They are non-degradable in waters and remain present for long periods of time and need to be carefully monitored (Buschmann et al., 2008). The groundwater sources were affected by seepage along the stream, and the apparent surface water–groundwater interactions which have been influencing the spatial distribution of trace metals. Surface water and groundwater interaction involve the exchange of water masses between the surface and the soil, the alteration of the physical, chemical, biological and energetic properties of the water bodies involved, and the prevailing ground characteristics and environment conditions. The compressibility, viscosity and density of different water bodies can be considered as constant in the interaction cases; sometimes. However, the differences in density became fundamental, due to the differing temperatures. There is a difference in chemical and microbiological characteristics between surface water and groundwater. Energetic conditions and the consequent conditions of motion, governed the interactions and exchanges between surface water and groundwater bodies. Exchange between surface water and groundwater can happen in the event of direct contact between superficial water and an aquifer where there is a common hydraulic head. More often, however, the exchange happens through series of levels of unsaturated soil, while two water bodies have independent hydraulic characteristics and motion. The unsaturated level varies according to the climatic conditions and to the levels of the strata involved. (Cavazza, Pagliara, 2009)

3.5 Adsorption Capacity

For strongly adsorbed solutes of limited solubility, the value of the amount of adsorbed substance reached in a saturated solution is called the adsorption capacity of the adsorbent for a specific solute; its value depends also, in general, on the nature and, in the case of more than two components, on the relative composition of the bulk liquid. Clay soil has a high adsorption capacity comparing to other types of soil. (IUPAC, 1997)

3.6 Soil Column Study

For over a century, soil column study has been used in the study of hydrogeological properties. (Darcy, 1856). Recently, soil columns have been used to execute transport models, to assess the fate and mobility of contaminants in soil and for evapotranspiration studies. There is considerable variation in the soil columns which have been reported in the literature. Some of the smallest size 1cm diameter and a length of 1.4 cm. While some of the largest size 2m*2m *5m had been used. And others which have been used in heavy metals transportation in soil were: 5 cm internal diameter and a length of 31 cm and 18,6 cm inner diameter and a height of 62 cm. (Lewis and Sjöstrom, 2010).

Recent study identified the limitations of column size with an inner diameter of at least 4 cm and a minimum height of 20 cm. Soil repacking is one of the most important issue in soil column experiment, because it restores the bulk density of the soil to a value similar to that observed naturally and to avoid the formation of cracks. There are two common ways for soil repacking in the column which are: dry or wet and slurry repacking. The first one involves loading small discrete amounts of dry or wet soil into the column and then packing it mechanically either by hand or pestle. while the second one involves saturating the soil with an excess of water. Columns made of suitably solid materials like glass, stainless steel, aluminum, Teflon and PVC, then packed with soil and afterwards saturated and equilibrated with an “artificial rain” solution which allowed to drain and finally collecting the leachate. After the leaching process the soil samples were collected from the columns at different depths depending on the information required from the study. Each soil and leachate samples are analysed for the test substance and, if it is appropriate, for transformation products or other chemicals of interest. (OECD, 2004).

3.7 Summary

Heavy metals are toxic substances that causes such a big harm to the living creatures if exceeded the allowed level of concentration in the environment. The industrial and agricultural actions are the main reasons of the increase in concentrations level of heavy metals in soil and water, also there are some factors that affect the mobility of heavy metals in soil and enhance its transportation from surface to groundwater through the interaction between them.

As a result this research is wide important to do in Faria catchment since it has an intensive agricultural activities and due to the effect of the industrial waste from the east of Nablus, those are the main sources of heavy metals that threat the quality of groundwater their. This research consider the case of heavy metals transport from stream into soil and groundwater using column study expriment.

Chapter Four

Data Collected and Analysis Methodology

Chapter Four

Data Collected and Analysis Methodology

4.1 Research Methodology

To achieve the objectives of this study, ArcGIS software, Ms-Excel software and Laboratory analysis were used to explain and illustrate different data. **Figure 4.1** describes the overall methodology which was used in this research.

The following summarize the main steps that were followed:

1- Sampling and data collection
   - Collecting surface water, soil at three different depths and groundwater samples from 6 locations at two times in dry and wet seasons in Faria catchment.

2- Laboratory analysis
   - Soil samples were digested using aqua regia (ISO 11466.3 method) method.
   - By Using ICP/MS instrument, the concentrations of Cr, Ni, Cu and Cd were determined in all collected samples.
   - Execute the column study on soil sample.

3- Data management
   - The analyzed results of concentrations will be compared with standards.
   - Constructing heavy metals profile in stream water, soil and groundwater.

- Analyze the results of column study experiment.

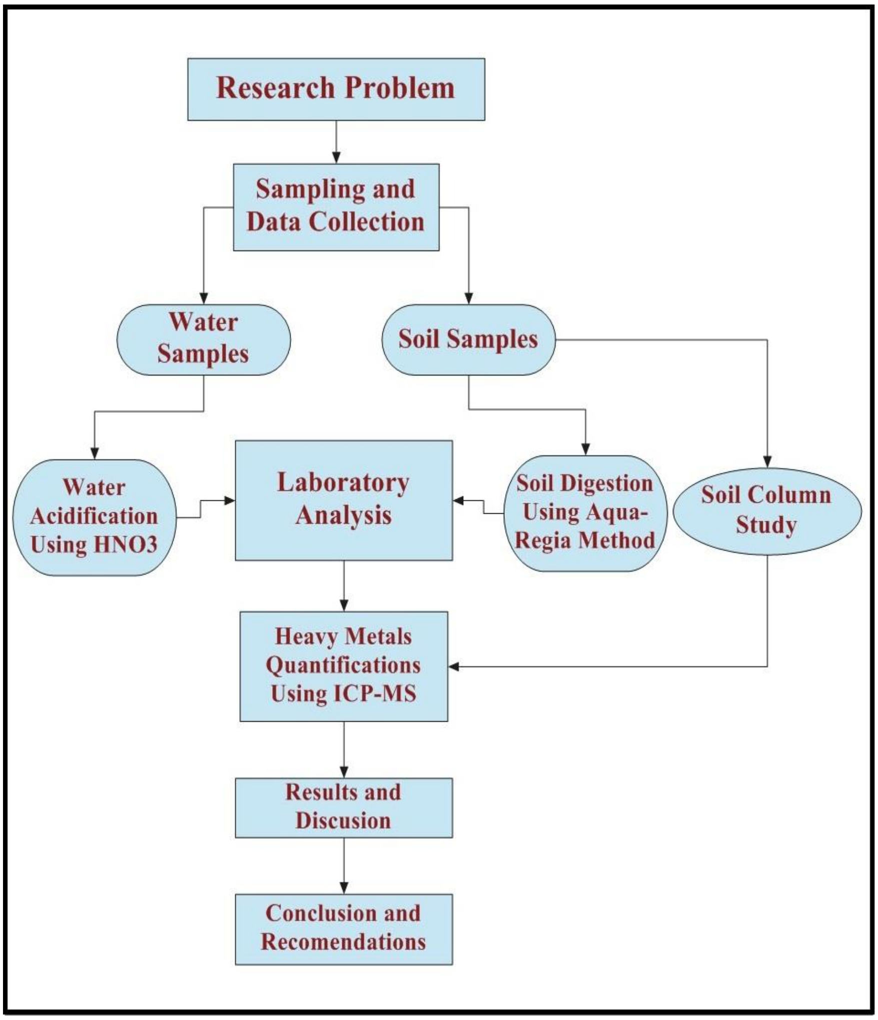


Figure 4.1: Methodology Flowchart

4.2Collecting Samples

To assess the transport of heavy metals from wadi AlFaria stream into soil and ground water, six locations were selected, each one represents a groundwater well, depending on the availability and vicinity to wadi Al-Faria stream as following in **Table 4.1, Figure 4.3** shows the distribution of these locations along wadi Al-Faria.

Table 4.1: Locations in Faria catchment from which the samples had been taken

Location No.	Owner Name	Well No.
Location1	Qasem 'Abed Al Hadi	18-18/034
Location2	Nader 'Abed Al Hadi	18-18/027
Location3	Hafedh 'Abdallah	18-18/035
Location4	Samirah 'Abed Al Hadi	18-18/031A
Location5	Khaleel 'Abed Al Hadi	18-18/036
Location6	Ibraheem Hamdan	18-18/039

Two types of samples were collected: water and soil, (as shown in **Figure 4.2)** in dry (in June) and wet (in January) seasons. The rainy season, is the time of year when most of a region's average annual rainfall occurs. It usually lasts one or more months. The dry season is a yearly period of low rainfall, the dry season has low humidity, and some watering holes and rivers dry up. (Alvares, et al., 2013)

Five samples were taken from each location:

1- A Surface water sample from wadi AlFaria stream.
2- A Groundwater sample from the well.
3- Three soil samples from three different depths as the following: 0-10 cm, 10-30 cm, 30-50 cm. They have been picked near the stream directly.

Figure 4.2: Samples (Soil, Groundwater and Surface Water)

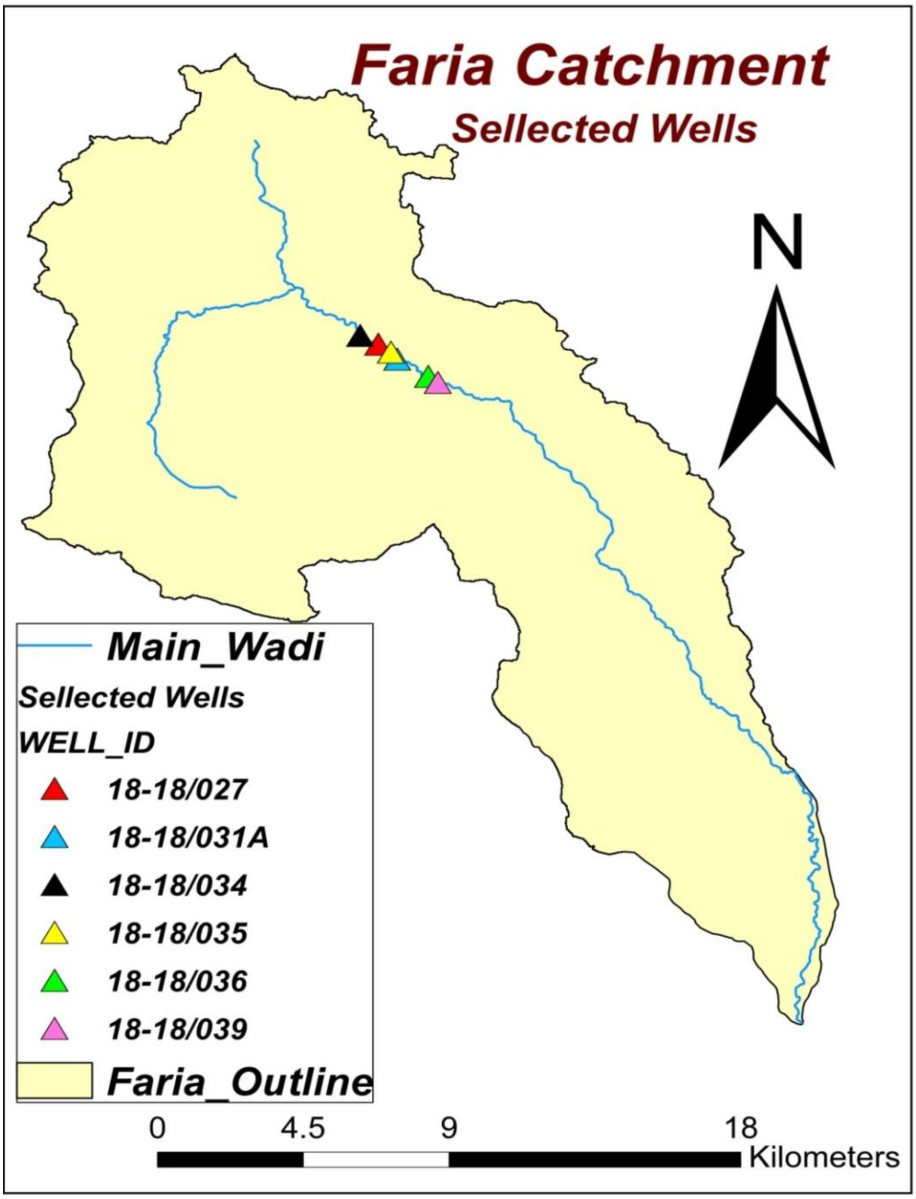


Figure 4.3: The Selected Wells From Al-Faria Catchment

4.3 Laboratory Analysis

To know the concentrations of Ni, Cu, Cr and Cd in all samples, Inductively Coupled Plasma Mass Spectrometry or ICP-MS technique was used, the samples were quantified by ICP-MS as triplicate. Some preparations were made for the soil and water samples before the ICP-MS analysis. **Figure 4.4** shows laboratory analysis for water and soil samples.

4.3.1 Water sample

Water samples include wadi Al Faria stream water and groundwater wells: 1 ml of concentrated nitric acid was added to 100 ml of water sample (Agilent Technology, 2005), then they were ready to be analyzed by ICP-MS.

4.3.2 Soil Samples

Soil samples had been digested using Aqua Regia (ISO 11466.3 method): Around 0.25 g of soil were accurately weighted and placed in a 250 ml Pyrex Erlenmeyer flask. First, the pre-digestion step was done at room temperature for 24 h with 10 ml of a (3:1) mixture of 12 M HCl and 17 M HNO_3. Then, the suspension was digested on hotplate at 130 °C for 15 min. The obtained suspension was cooled to room temperature, filtered through an ashless Whatman 41 filter and, finally, diluted to 25 ml with 0.17 M HNO_3.(Peña-Icart, et al, 2011)

Figure 4.4: Laboratory Analysis

4.4 Column Study Experiment

Six PVC columns were prepared (PVC column is an available material), each one has a length of 70cm, 6 inchs in diameter and filled with 30cm depth of soil, which were collected from AlFaria catchment see **Annex B**, which represents soil profile at sampling location. The columns were classified into 3 groups as the following:

1- Two columns represent the concentrations of heavy metals for 5years.
2- Two columns represent the concentrations of heavy metals for 10years.
3- Two columns represent the concentrations of heavy metals for 20years.

Two columns were used for each concentration in order to make the experiment more accurate.

Firstly, the soil was repacked by infiltrated the columns with tap water for 24 hours, then blank water sample was taken from the effluents. Secondly, each column was infiltrated with 75 litres of water that contained Ni, Cd, Cu and Cr at different concentrations for each column group as illustrated in **Table 4.2** during 24hours,then water samples were taken from the effluents once per four hours. **Figure 4.5**Shows the setup of column Experiment. Finally, soil samples were collected from each column at three different depths: top, middle and bottom of the column as shown in **Figure 4.6.**

All samples (Soil and water) were prepared and analysed by ICP-MS as mentioned previously in section 4.2 to quantify Ni, Cd, Cu and Cr concentrations. **Figure 4.7**shows the laboratory analyzation for soil and water samples.

Figure 4.5: Column Experiment Setup.

Figure 4.6: The Three Different Depths where Soil Samples Were Taken

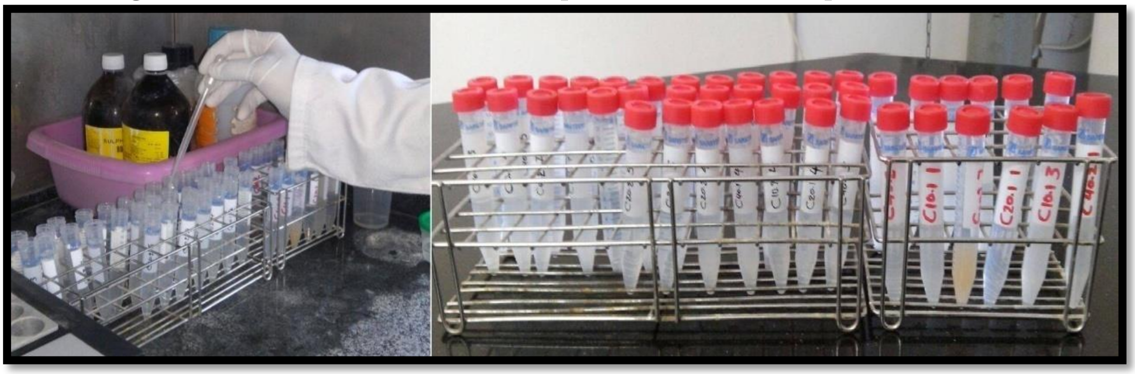


Figure 4.7: Laboratory Analysis for Column Study Samples

Inflow Calculations

Inflow:

Q = Velocity*Area

Velocity = Hydraulic conductivity* Hydraulic gradient

Hydraulic conductivity for the soil in Wadi AlFaria catchment = 0.143 m/d (Homeidan, 2013).

The average depth of water in wadi Al-Faria (ΔH) = 0.08 m (Alawneh, 2013).

The height of water in the column (ΔL) = 0.5 m

Hydraulic gradient = $\Delta H/\Delta L$ = 0.08/0.5 = 0.16

Velocity = 0.0228 m/d

Diameter of the column = 6 inch, cross sectional Area = 0.018 m^2

Q = 150 L/yr

If Considering 75 L/yr to simulate the flow since 150 L/yr is a large amount, therefore the concentrations of heavy metals in the inflow was determined as follow:

150 L/yr * C = 75 L/yr * X

C: Average concentration of heavy metals in wadi AlFaria stream in dry and wet seasons.

X = 2C

The concentrations of heavy metals for 5 yr = 5X = 10C

The concentrations of heavy metals for 10 yr = 10X = 20C

The concentrations of heavy metals for 20 yr = 20X = 40C

Table 4.2: The Concentrations of Ni, Cd, Cr and Cu In The Inflow For Different Column Groups (ppb).

Element	Ni	Cd	Cr	Cu
C=Avg. Dry and Wet	8.95	0.077	7.86	3.16
5yr Conc. =10C	89.53	0.77	78.60	31.67
10yr Conc. =20C	179.07	1.54	157.20	63.35
20yr Conc. =40C	358.14	3.08	314.41	126.70

Chapter Five

Results and Discussion

Chapter Five

Results and Discussion

5.1 Introduction

All possible results which were obtained after doing the previously mentioned methodology are listed and discussed in this chapter, and that includes heavy metals concentrations profile in dry and wet seasons for the six selected locations, also the results were gained from column study experiment such as outflow concentrations, accumulation of heavy metals in soil for Nickel, Copper, Cadmium and Chromium. Then the relations between the data were established using Ms-Excel software.

5.2 Heavy Metals Concentrations Profile in Dry and Wet Seasons

In general, Ni, Cd, Cu and Cr were detected at all locations in all samples, the concentrations of these heavy metals are very low compared to maximum permissible limits that shown in **Table 5.1**. In wet season the concentrations are less than in dry season due to the dilution caused by rain water for stream, soil and groundwater. Also, the average concentrations of heavy metals in a descending order are as the following:

soil > surface > groundwater. **Annex A** shows all the concentrations for the selected heavy metals in dry and wet seasons. The Dilution caused by rain water was measured using dilution factor (DF) = Concentration in dry / Concentration in wet

All concentrations were measured in part per billion (ppb)

Table 5.1: Permissible Limits of Heavy Metals in Water (EPA, 2009) and Soil(US EPA, 2002).

Element	Recommended maximum concentration in water (ppb)	Recommended maximum concentration in Soil (ppb)
Cd (Cadmium)	5	70,000
Cr (Chromium)	100	230,000
Cu (Copper)	1300	270,000
Ni (Nickel)	100	160,0000

5.2.1 Nickel

Figures 5.1 and 5.2depicts the concentrations of Ni in dry and wet seasons. The Ni average concentrations for surface water, groundwater and soil in wet season are less than in dry season as shown in **Table 5.2**. The maximum Ni concentration in water samples (wither ground water or stream water) was 12.84 ppb which is much less than the maximum recommended concentration that equals 100 ppb. Also the same thing was with the soil samples , the maximum concentrations of Ni (48.30 ppb) is much less than the maximum recommended concentrations (160,0000 ppb).That means the concentrations of Nickel in Faria catchment doesn't harm the living things there in the current time.

Table 5.2: Average Nickel Concentrations in Dry and Wet Seasons

Nickel	Avg. Conc. in Wet Season (ppb)	Avg. Conc. in Dry Season (ppb)	Dilution Factor DF
Surface	5.06	**12.84**	2.53
Soil 0-10 cm	32.59	**48.30**	1.48
Soil 10-30 cm	41.03	**47.78**	1.16
Soil 30-50 cm	43.11	**48.11**	1.11
Well	2.34	**10.93**	4.67

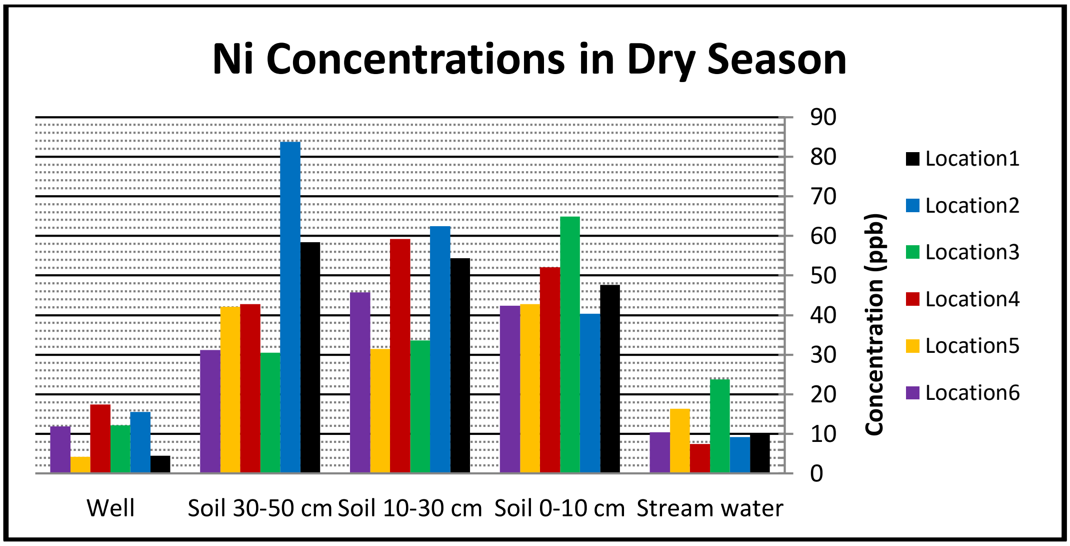


Figure 5.1: Nickel Concentrations in Dry Season.

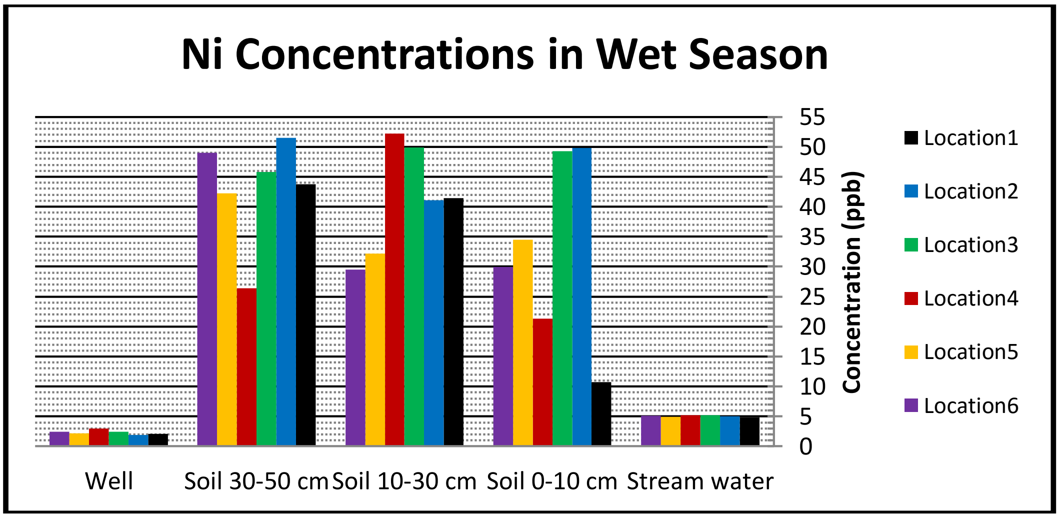


Figure 5.2: Nickel Concentrations in Wet Season.

5.2.2 Cadmium

Figures 5.3 and 5.4 depicts the concentrations of Cd in dry and wet seasons. The Cd average concentrations for surface water, groundwater and soil in wet season are less than in dry season as shown in **Table 5.3**. The maximum Cd concentration in water samples (wither ground water or stream water) was 0.137 ppb which is much less than the maximum recommended concentration that equals 5 ppb. Also the same thing was with the soil samples, the maximum concentrations of Cd (1.470 ppb) is much less than the maximum recommended concentrations (70,000 ppb). That means the concentrations of Cadmium in Faria catchment don't harm the living things there in the current time.

Table 5.3: Average Cadmium Concentrations in Dry and Wet Seasons

Cadmium	Avg. Conc. in Wet Season (ppb)	Avg. Conc. in Dry Season (ppb)	Dilution Factor DF
Surface	0.06	**0.09**	1.63
Soil 0-10 cm	0.52	**0.60**	1.16
Soil 10-30 cm	0.88	**0.81**	0.92
Soil 30-50 cm	1.47	**0.72**	0.49
Well	0.05	**0.14**	2.98

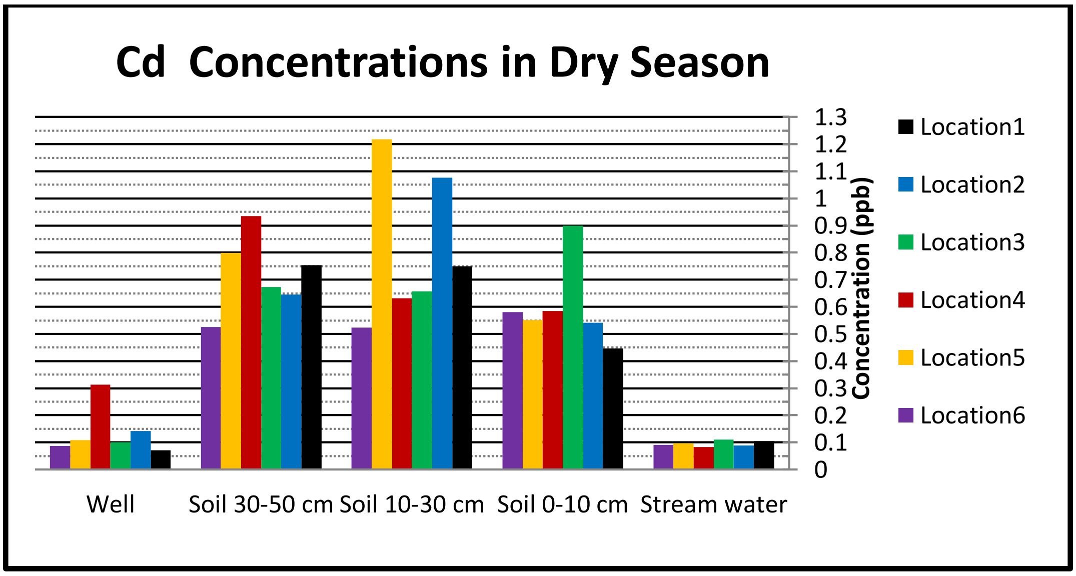


Figure 5.3: Cadmium Concentrations in Dry Season.

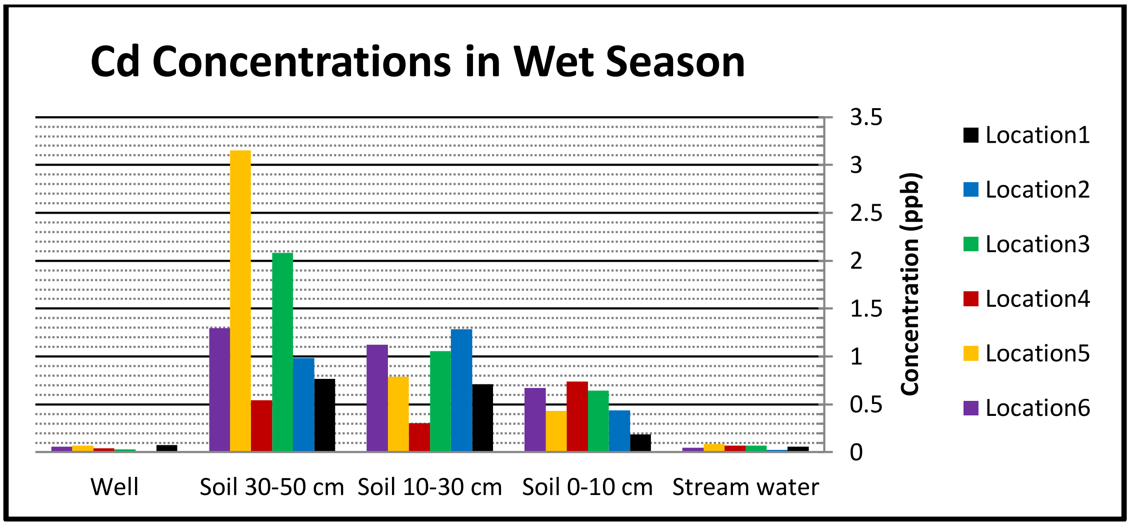


Figure 5.4: Cadmium Concentrations in Wet Season.

5.2.3 Copper

Figures 5.5 and 5.6depicts the concentrations of Cu in dry and wet seasons. The Cu average concentrations for surface water, groundwater and soil in wet season are less than in dry season as shown in **Table 5.4**. The maximum Cu concentration in water samples (wither ground water or stream water) was 4.60 ppb which is much less than the maximum recommended concentration that equals 1300 ppb. Also the same thing was with the soil samples , the maximum concentrations of Cu (45.21 ppb) is much less than the maximum recommended concentrations (270,000 ppb). That means the concentrations of Copper in Faria catchment don’t harm the living things there in the current time.

Table 5.4: Average Copper Concentrations in Dry and Wet Seasons

Copper	Avg. Conc. in Wet Season (ppb)	Avg. Conc. in Dry Season (ppb)	Dilution Factor DF
Surface	2.42	**3.91**	1.62
Soil 0-10 cm	27.31	**40.53**	1.48
Soil 10-30 cm	37.55	**45.21**	1.20
Soil 30-50 cm	32.09	**34.07**	1.06
Well	3.97	**4.60**	1.16

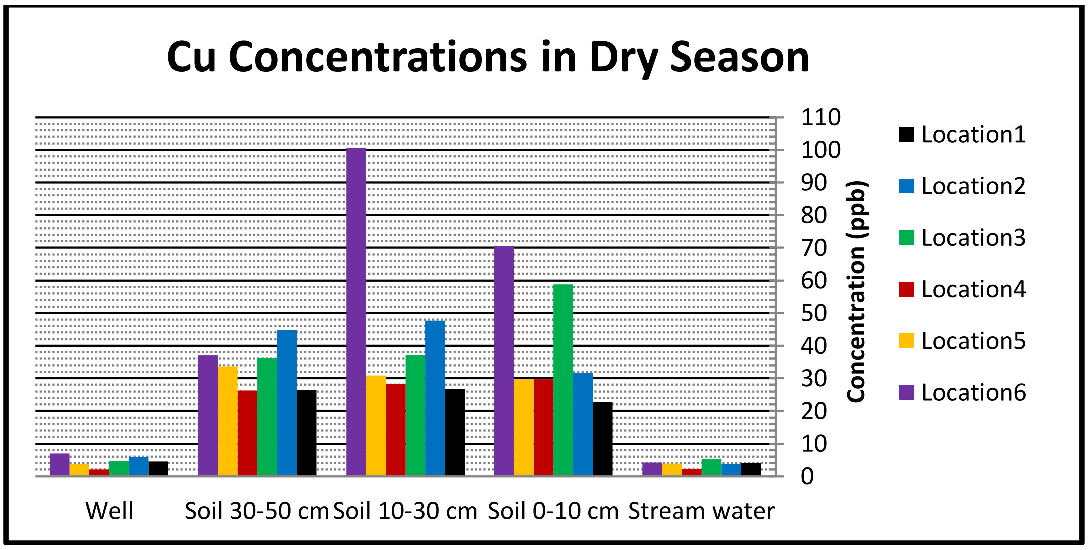


Figure 5.5: Copper Concentrations in Dry Season.

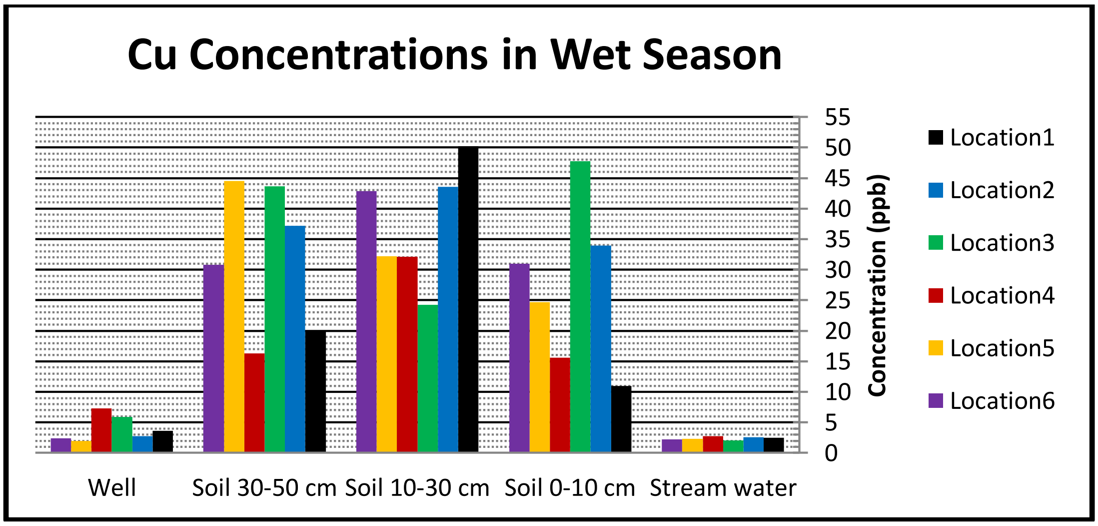


Figure 5.6: Copper Concentrations in Wet Season.

5.2.4 Chromium

Figures 5.7 and 5.8 depicts the concentrations of Cr in dry and wet seasons. The Cr average concentrations for surface water, groundwater and soil in wet season are less than in dry season as shown in **Table 5.5.**The maximum Cr concentration in water samples (wither ground water or stream water) was 9.17 ppb which is much less than the maximum recommended concentration that equals 100 ppb. Also the same thing was with the soil samples, the maximum concentrations of Cr (55.55 ppb) is much less than the maximum recommended concentrations (230,000 ppb). That means the concentrations of Chromium in Faria catchment don't harm the living things there in the current time.

Table 5.5: Average Chromium Concentrations in Dry and Wet Seasons

Chromium	Avg. Conc. in Wet Season (ppb)	Avg. Conc. in Dry Season (ppb)	Dilution Factor DF
Surface	6.55	**9.17**	1.40
Soil 0-10 cm	35.50	**55.55**	1.56
Soil 10-30 cm	44.38	**50.80**	1.14
Soil 30-50 cm	42.01	**43.70**	1.04
Well	4.83	**7.45**	1.54

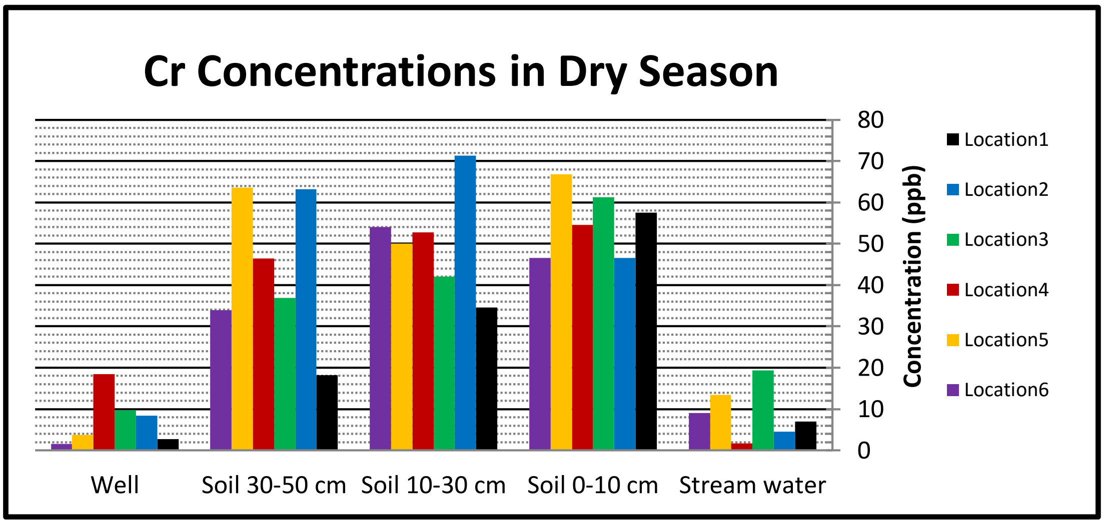


Figure 5.7: Chromium Concentrations in Dry Season.

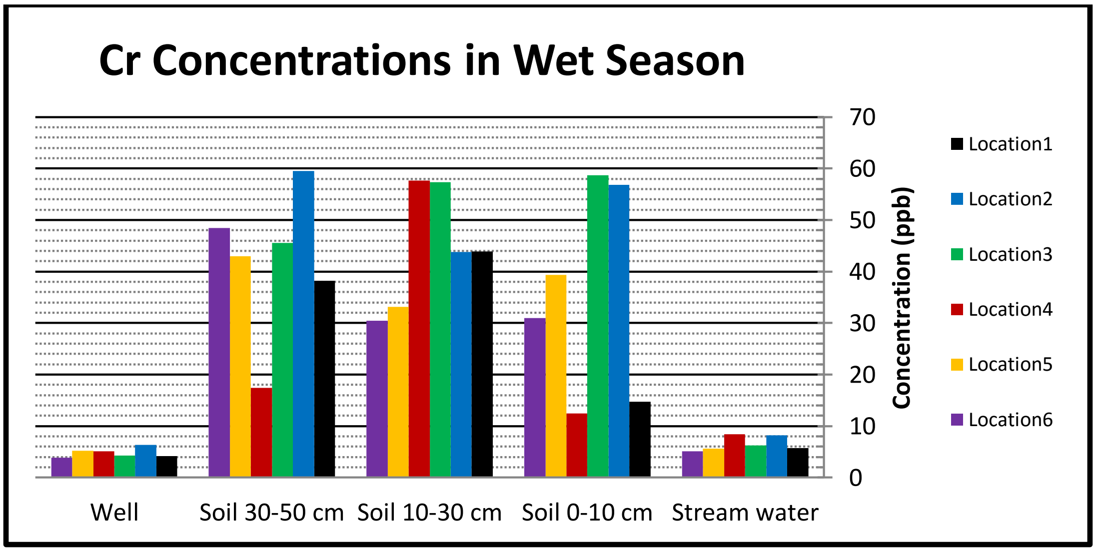


Figure 5.8: Chromium Concentrations in Wet Season.

5.3 Statistical Analysis

Statistical analysis including mean, median, standard deviation, maximum and minimum concentrations were carried out for all samples at the six selected locations. **Table 5.6** gives the general statistical measures computed for the concentrations results of Ni, Cd, Cu and Cr. The values of standard deviation was large with respect to average, due to the large variation in the concentrations of heavy metals as obtained from maximum and minimum values.

In addition, data obtained was subjected to the analysis of variance (ANOVA). A probability ≤ 0.05 was considered as significant. **Table 5.7** shows the significant level values for the selected heavy metals in wet and dry seasons.

ANOVA showed that the significant level (p-value) for the selected heavy metals in dry and wet season are > 0.05, so there is no significant variation in the concentrations of Ni, Cd, Cu and Cr with the sampling locations in dry and wet season.

Table 5.6:General Statistical Measures Computed for Ni, Cd, Cu and Cr Concentrations Results In Wet and Dry Seasons.

Dry Season						
Element	Parameter	Mean	Median	St. Dev σ	Max.	Min.
Ni	Surface	12.84	10.10	6.16	23.81	7.46
	Soil 0-10 cm	48.30	45.17	9.14	64.81	40.30
	Soil 10-30 cm	47.79	50.02	13.13	62.49	31.41
	Soil 30-50 cm	48.12	42.44	20.15	83.69	30.51
	GW	10.93	11.97	5.53	17.46	4.25

Cd	Surface	0.096	0.094	0.010	0.110	0.083
	Soil 0-10 cm	0.601	0.567	0.155	0.899	0.446
	Soil 10-30 cm	0.810	0.703	0.275	1.219	0.524
	Soil 30-50 cm	0.722	0.714	0.141	0.935	0.525
	GW	0.137	0.105	0.090	0.314	0.071
Cu	Surface	3.91	3.97	1.00	5.42	2.28
	Soil 0-10 cm	40.53	30.70	19.33	70.63	22.72
	Soil 10-30 cm	45.22	34.00	28.18	100.57	26.81
	Soil 30-50 cm	34.08	34.99	7.04	44.75	26.29
	GW	4.61	4.55	1.66	6.92	2.10
Cr	Surface	9.17	8.04	6.37	19.31	1.68
	Soil 0-10 cm	55.55	56.03	8.06	66.82	46.54
	Soil 10-30 cm	50.80	51.41	12.42	71.24	34.60
	Soil 30-50 cm	43.70	41.65	17.75	63.56	18.23
	GW	7.45	6.11	6.31	18.50	1.57
Wet Season						
Ni	Surface	5.06	5.07	0.15	5.24	4.87
	Soil 0-10 cm	32.59	32.21	15.44	49.80	10.69
	Soil 10-30 cm	41.03	41.23	9.11	52.20	29.52
	Soil 30-50 cm	43.11	44.77	8.86	51.47	26.39
	GW	2.34	2.29	0.39	3.01	1.87
Cd	Surface	0.06	0.02	0.09	0.03	0.06
	Soil 0-10 cm	0.54	0.21	0.74	0.19	0.52
	Soil 10-30 cm	0.92	0.35	1.28	0.30	0.88
	Soil 30-50 cm	1.14	0.98	3.15	0.54	1.47
	GW	0.05	0.03	0.08	0.00	0.05
Cu	Surface	2.42	2.41	0.26	2.78	2.07
	Soil 0-10 cm	27.31	27.81	13.31	47.73	10.94

	Soil 10-30 cm	37.55	37.57	9.58	50.24	24.27
	Soil 30-50 cm	32.09	33.98	11.91	44.53	16.32
	GW	3.97	3.16	2.15	7.31	1.93
Cr	Surface	6.55	6.00	1.39	8.39	5.09
	Soil 0-10 cm	35.50	35.12	19.94	58.72	12.47
	Soil 10-30 cm	44.38	43.87	11.54	57.66	30.43
	Soil 30-50 cm	42.01	44.27	14.00	59.47	17.40
	GW	4.83	4.70	0.93	6.39	3.86

Table 5.7: P-Values for Ni, Cd, Cu and Cr in Dry and Wet Season .

Season	Heavy metals	Ni	Cd	Cu	Cr
Dry	p-Value	0.915	0.355	0.479	0.920
Wet	p-Value	0.958	0.797	0.952	0.823

5.4 Column Study Result

The fate of heavy metals in soil and the possibility of groundwater pollution is still a great environmental issue. However, heavy metals transport is defined as a very complicated problem. Column leaching experiments can quantitatively predict adsorption and transportation of different soil pollutants over a range of different inflow concentrations.

The results of the experiment for each two columns are having the same inflow concentrations were almost close, that confirms the accuracy of the work was quite good. **Annex C** shows tabulated results for the outflow of the experiment.

The percentage of removed heavy metal was calculated by the following formula (Mirzaei et al, 2013):

$E = \frac{Ci - Ce}{Ci} * 100\%$where Ci is the metal concentration in the influent sample in ppb and Ce is the metal concentration in the effluent sample in ppb.

5.4.1 Outflow Volume

For each column, the total inflow and outflow volumes over the experimental period were almost equal, indicating that water balance was achieved.

The outflow rate = $\left(\frac{Total\ Volume\ of\ Outflow}{Total\ Volume\ of\ Inflow}\right) * 100\%$

Total Volume of inflow per each four hours = 3 L and the average total outflow = 2.5 L

The outflow rate = 83.3% for each column. The "lost" volume may remained in the column or evaporated.

At the end of the experiment, it is notable that Ni, Cd, Cu and Cr concentrations in the outflow tend to be decreased with time in all different columns. In addition, the values of removal heavy metals by soil at different inflow concentrations were almost close that means adsorption capacity for soil is high, and not reach the saturation condition. As mentioned previously Al Faria soil is clay and clay loam, the adsorption capacity is high in this type of soil.

5.4.2 Nickel

The Ni concentration changes in the leachat at different inflow concentrations along the experiment period that are shown in **Figures 5.9, 5.10 and 5.11.** For the 5yr, 10yr and 20yr columns, the average Ni concentrations in the outflow during experiment time are: 15.33, 12.92 and 27.26 ppb, respectively. These are very small values when compared with inflow values which were 89.53 , 179.07 and 358.14 ppb respectively, and that appeared in the reduction mean percentages as illustrated in **Table 5.8**. Also, when considering the average Ni concentration in the outflow of blank column during 24hr which equals 12.7 ppb, it has been concluded that most of Ni amount which was added with the inflow for the different column types was adsorbed by soil. Therefore, Nickel transport was through soil and very small amounts were released with the outflow.

Table 5.8: The Reduction Mean Percentage of Ni Concentration By Soil.

Ni	Column 5yr.1	Column 5yr.2	Column 10yr.1	Column 10yr.2	Column 20yr.2	Column 20yr.2
% Reduction	80.04	85.68	91.22	94.33	91.60	93.16
% Mean	**82.86**		**92.775**		**92.38**	

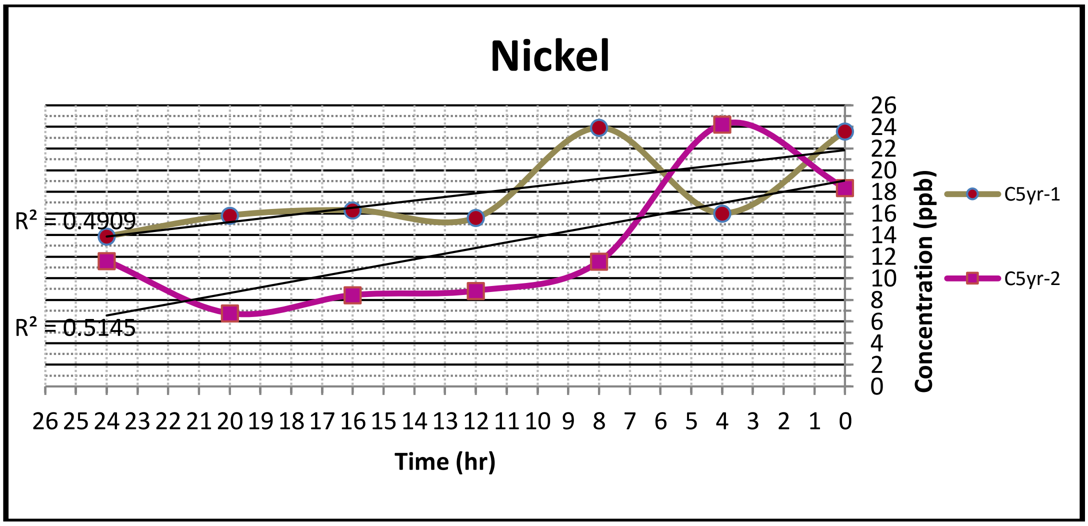


Figure 5.9: The Effluent Ni Concentration in Columns That Represent The Concentration of Heavy Metals for 5years With Time.

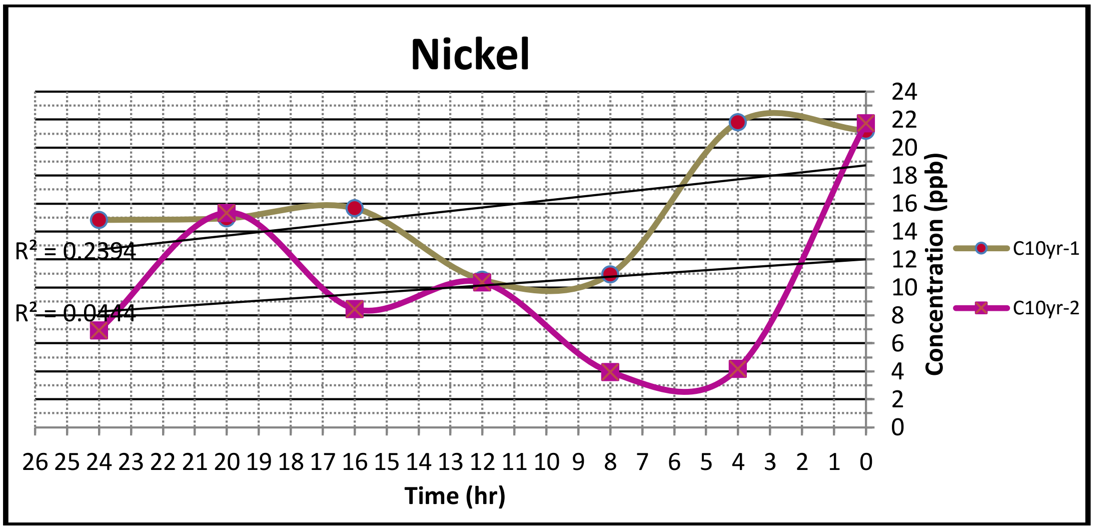


Figure 5.10: The Effluent Ni Concentration in Columns That Represent The Concentration of Heavy Metals for 10years With Time.

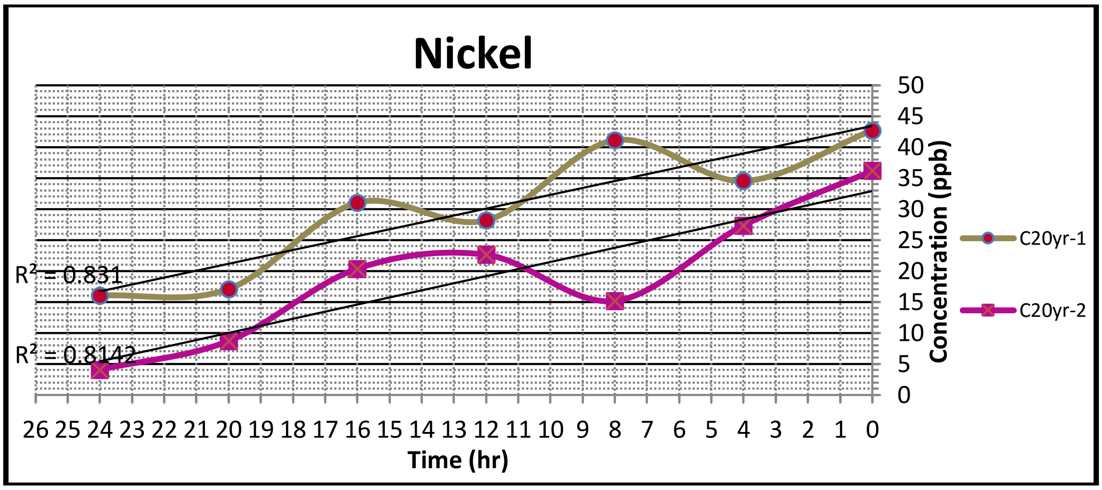


Figure 5.11: The Effluent Ni Concentration in Columns Represent The Concentration of Heavy Metals for 20 years With Time.

5.4.3 Cadmium

The Cd concentration changes in the leachat at different inflow concentrations along the experiment period that are shown in **Figures 5.12, 5.13 and 5.14.** For 5yr, 10yr and 20yr columns, the average Cd concentrations in the outflow during experiment time are: 0.092 , 0.105 and 0.14 ppb, respectively. These are very small values when compared with the inflow values which were 0.77, 1.54 and 3.08 ppb respectively, and that appeared in the reduction mean percentages as illustrated in **Table 5.9**. Also, when considering the average Cd concentration in the outflow of blank column during 24hr which equals 0.04 ppb, it has been concluded that most of Cd amount which was added with the inflow for different column types was adsorbed by soil. Therefore, Cadmium transport was through soil and very small amounts were released with the outflow.

Table 5.9: The Reduction Mean Percentage of Cd Concentration By Soil.

Cd	Column 5yr.1	Column 5yr.2	Column 10yr.1	Column 10yr.2	Column 20yr.1	Column 20yr.2
% Reduction	84.17	91.83	95.00	89.47	95.72	95.61
% Mean	88.00		92.23		95.67	

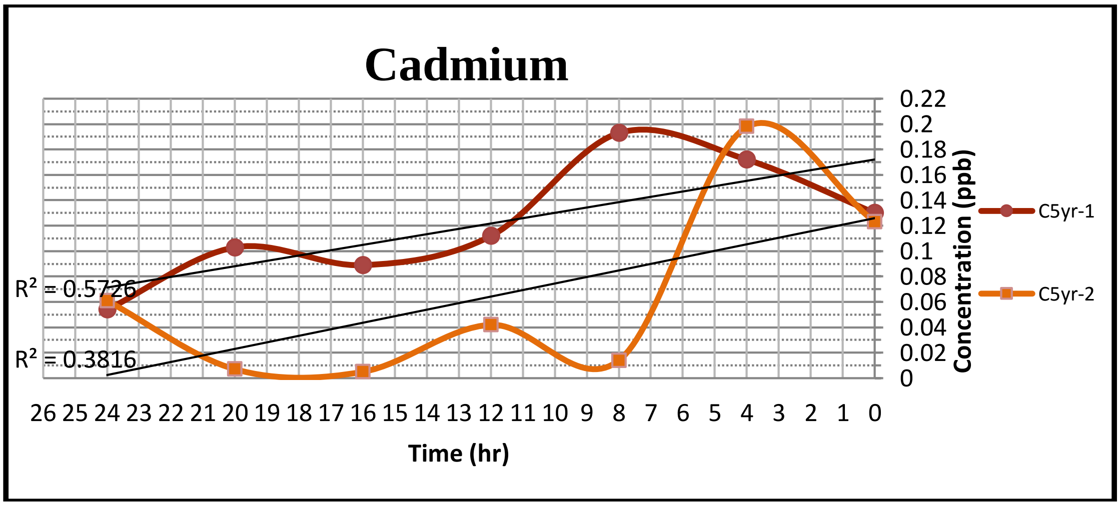


Figure 5.12: The Effluent Cd Concentration in Columns Represent The Concentration of Heavy Metals for 5years With Time.

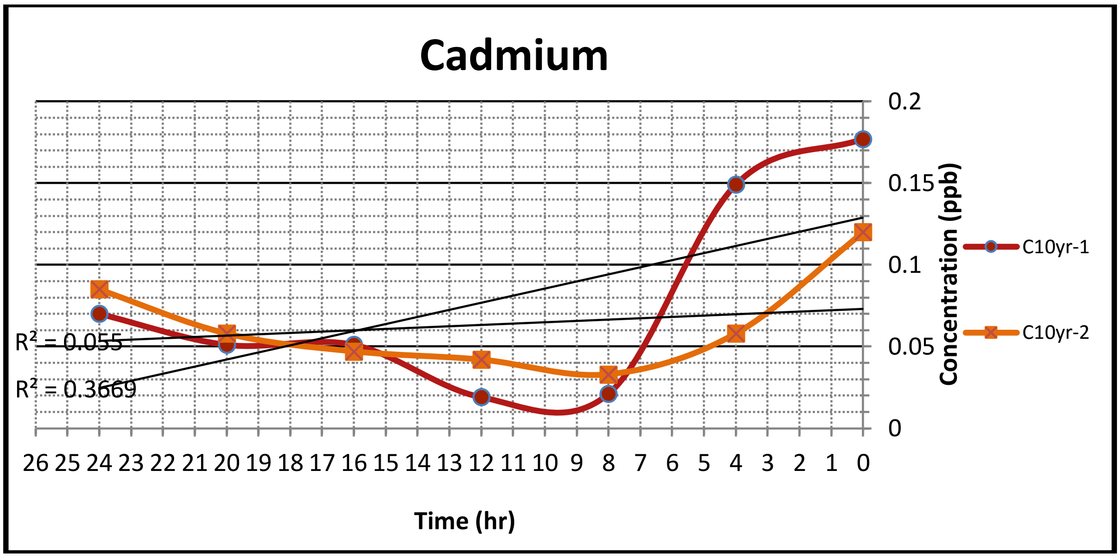


Figure 5.13: The Effluent Cd Concentration in Columns Represent The Concentration of Heavy Metals for 10years With Time.

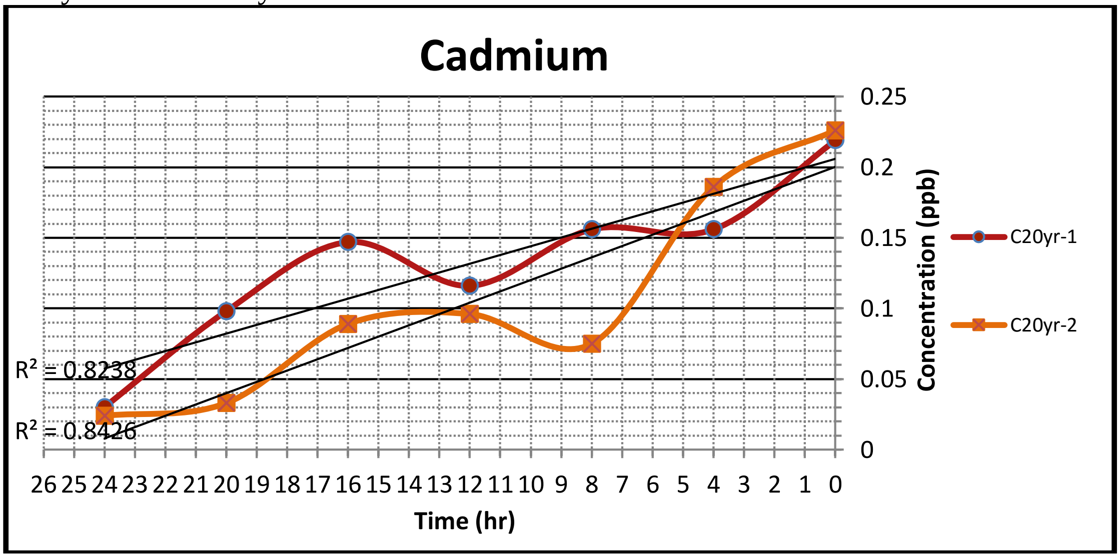


Figure 5.14: The Effluent Cd Concentration in Columns Represent The Concentration of Heavy Metals for 20years With Time.

5.4.4 Copper

The Cu concentration changes in the leachat at different inflow concentrations along the experiment period that are shown in **Figures 5.15, 5.16 and 5.17.** For 5yr, 10yr and 20yr columns, the average Cu concentrations in the outflow during experiment time are: 12.7, 9.04 and 16.6

ppb, respectively. These are small values when compared with the inflow values which were 31.67, 63.35 and 126.70 ppb respectively, and that appeared in the reduction mean percentages as illustrated in **Table 5.10**. Also, when considering the average Cu concentration in the outflow of blank column during 24hr which equals 17.4 ppb, it has been concluded that most of Cu amount which was added with the inflow for different column typeswas adsorbed by soil. Therefore, Copper transport was through soil and very small amounts were released with the outflow.

Table 5.10: The Reduction Mean Percentage of Cu Concentration By Soil.

Cu	Column 5yr.1	Column 5yr.2	Column 10yr.1	Column 10yr.2	Column 20yr.1	Column 20yr.2
% Reduction	56.28	63.13	81.77	89.64	87.94	85.82
% Average	**59.71**		**85.71**		**86.88**	

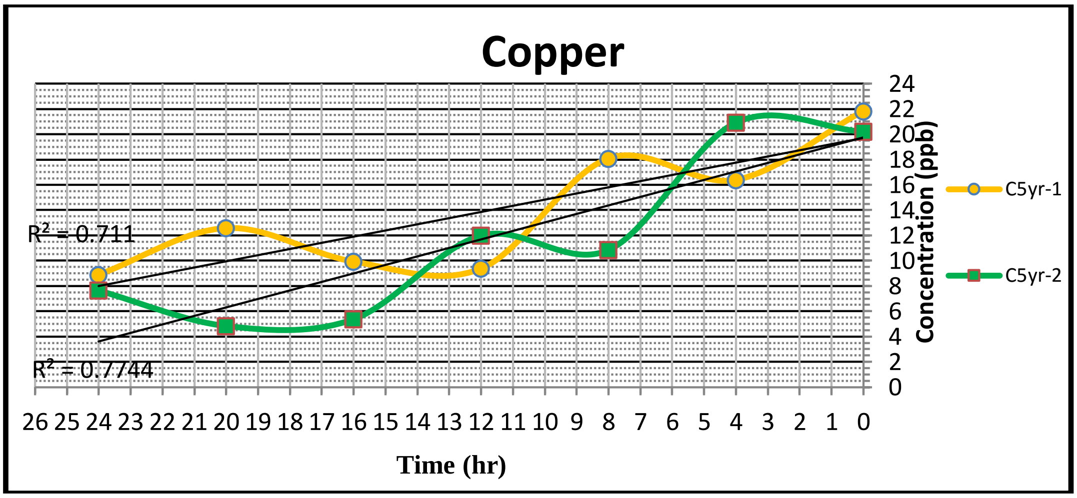


Figure 5.15: The Effluent Cu Concentration in Columns Represent The Concentration of Heavy Metals for 5 years With Time.

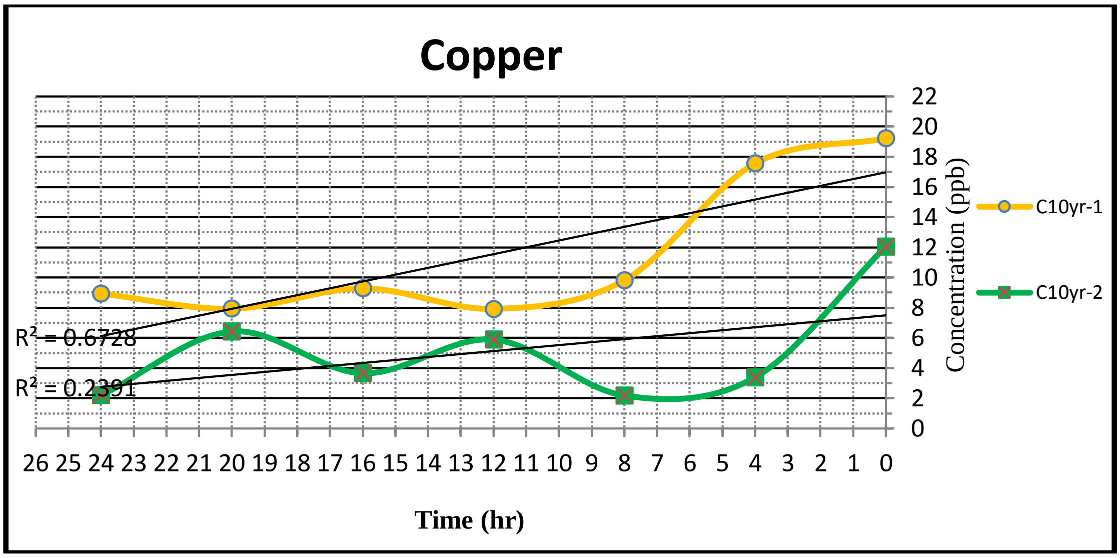


Figure 5.16: The Effluent Cu Concentration in Columns Represent The Concentration of Heavy Metals for 10years With Time.

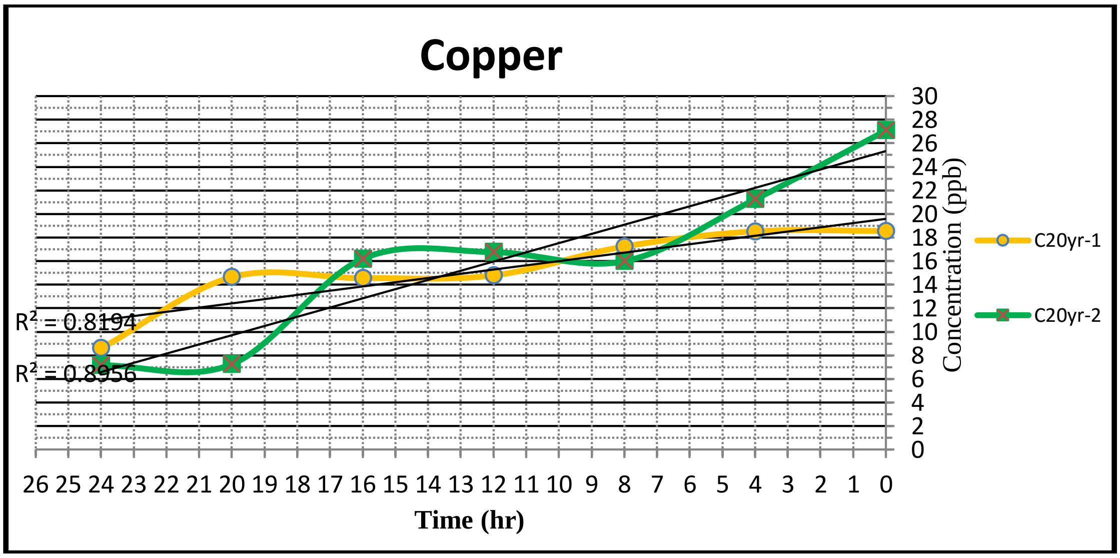


Figure 5.17: The Effluent Cu Concentration in Columns Represent The Concentration of Heavy Metals for 20years With Time.

5.4.5 Chromium

The Cr concentration changes in the leachat at different inflow concentrations along the experiment period that are shown in **Figures 5.18, 5.19 and 5.20.** For 5yr, 10yr and 20yr columns, the average Cr concentrations in the outflow during experiment time are: 13.11 , 12.49 and 25.05 ppb, respectively. These are very small values when compared with the inflow values which were 78.60 , 157.20 and 314.41 ppb respectively, and that appeared in the reduction mean percentages as illustrated in **Table 5.11** . Also, when considering the average Cr concentration in the outflow of blank column during 24hr which equals 6.18 ppb, it has been concluded that most of Cr amount which was added with the inflow for different column types was adsorbed by soil. Therefore, Chromium transport was through soil and very small amounts were released with the outflow.

Table 5.11: The Reduction Mean Percentage of Cu Concentration By Soil.

Cr	Column 5yr.1	Column 5yr.2	Column 10yr.1	Column 10yr.2	Column 20yr.1	Column 20yr.2
% Reduction	80.95	85.68	90.58	93.51	91.60	92.40
% Average	**83.31**		**92.05**		**92.03**	

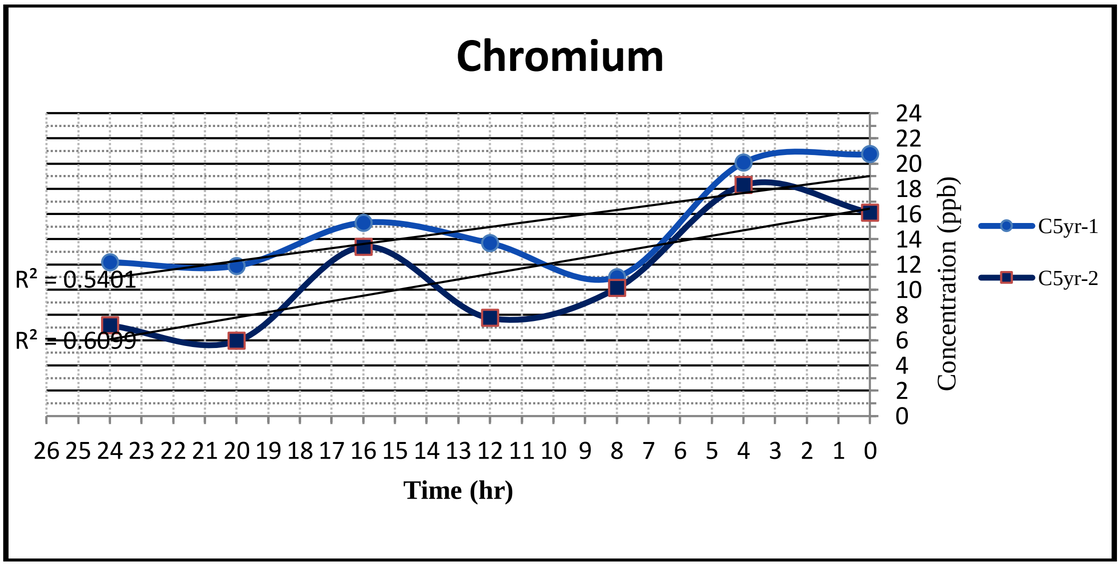


Figure 5.18: The Effluent Cr Concentration in Columns Represent The Concentration of Heavy Metals for 5 years With Time.

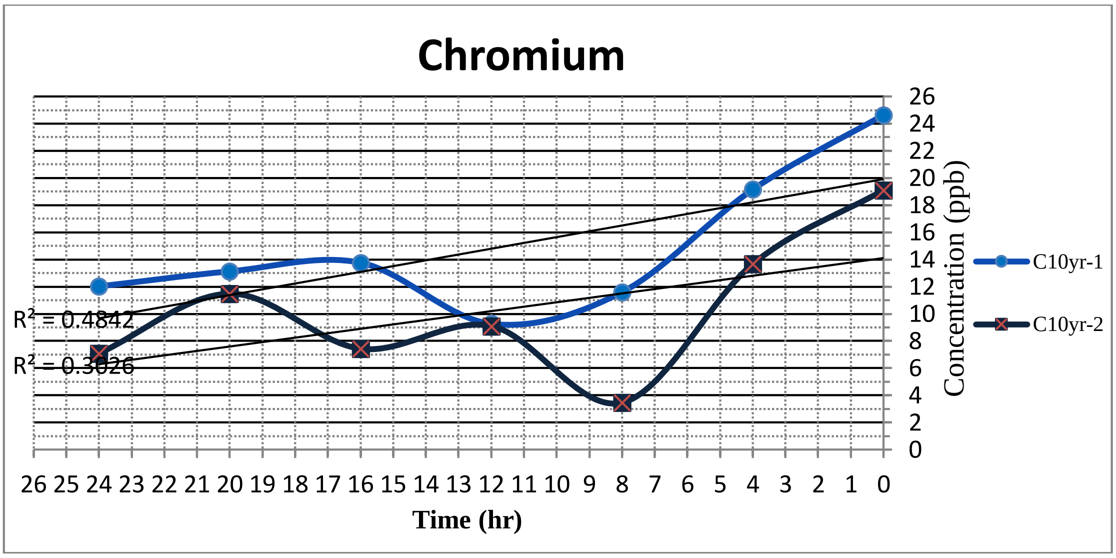


Figure 5.19: The Effluent Cr Concentration in Columns Represent The Concentration of Heavy Metals for 10 years With Time.

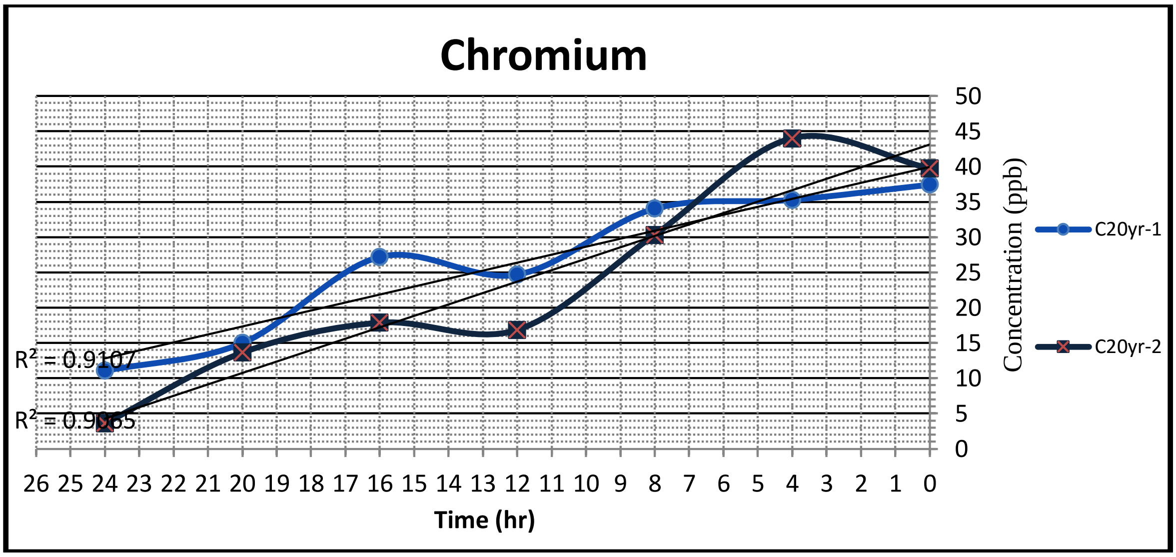


Figure 5.20: The Effluent Cr Concentration in Columns Represent The Concentration of Heavy Metals for 20 years With Time.

5.5Conclusion

According to the trend lines and R^2 values for Time-Concentration curves, it is notable that the relation tends to be linear (the concentration decreases with time) in the columns of 20yr-concentarions for all selected heavy metals (Ni, Cu, Cd and Cr). The change of concentration with time approaches to be negative constant and the concentrations tend to equal zero at long term of time.

5.6 Accumulation of Heavy Metals In Soil

Figures 5.21 and 5.22 show the concentration of Nickel, Copper, Cadmium and Chromium in the three layers: top at 0 cm depth, middle at 15 cm depth and bottom at 30 cm depth for the different columns concentrations (5yr-Conc., 10yr-conc. and 20-yr conc.).

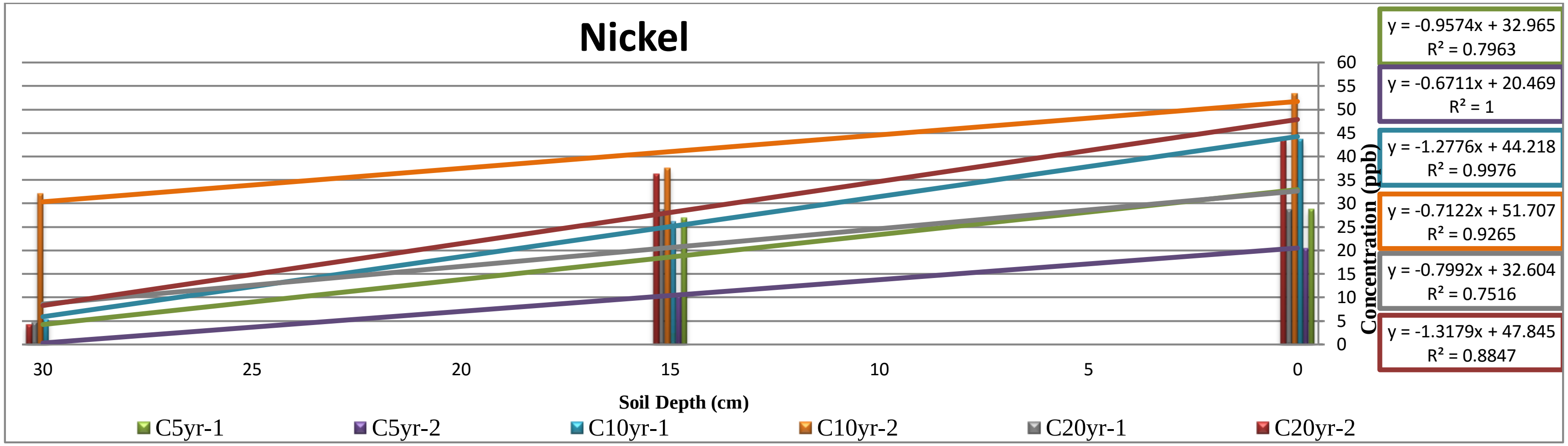
Most of Ni, Cu, Cd and Cr accumulated in the top and middle layers of the columns. According to R^2 values the concentration-depth relation is linear, when depth increases, the concentration decreases. That means the soil is homogeneous and heavy metals adsorption occurs.

From the equations of the trend lines, the depth at zero concentration was calculated. **Table 5.12**shows the average soil depth at which the concentrations become zero. In 5yr-conc columns the average depth at which the concentrations of Ni, Cu, Cd, and Cr become zero is equal to 32.97 cm, while in the 10yr-conc columns it equals to 48.10 cm and in the 20yr-conc columns 38.50 cm. From these results it can be concluded that the selected heavy metals were adsorbed by soil at little depth from the surface, and that enhance the idea of weak possibility for these heavy metals to reach and pollute groundwater.

Annex D shows tabulated results for the soil profile.

Table 5.12: Average Depth at Which the Concentrations of Ni, Cu, Cd and Cr Equal Zero.

Heavy Metals	5yr-Conc	10yr-Conc.	20yr-Conc
Ni	32.4 cm	53.6 cm	38.5 cm
Cu	33.2 cm	55.3 cm	34.6 cm
Cd	33.3 cm	38.1 cm	34.5 cm
Cr	33.0 cm	45.3 cm	46.4 cm
Average Depth	**32.97 cm**	**48.10 cm**	**38.50 cm**



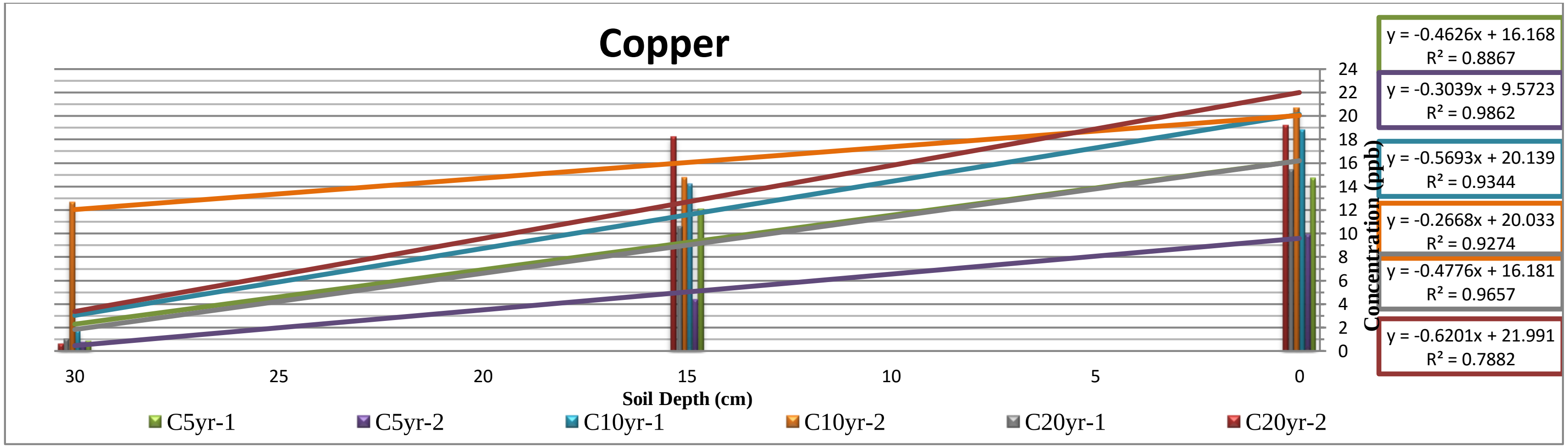
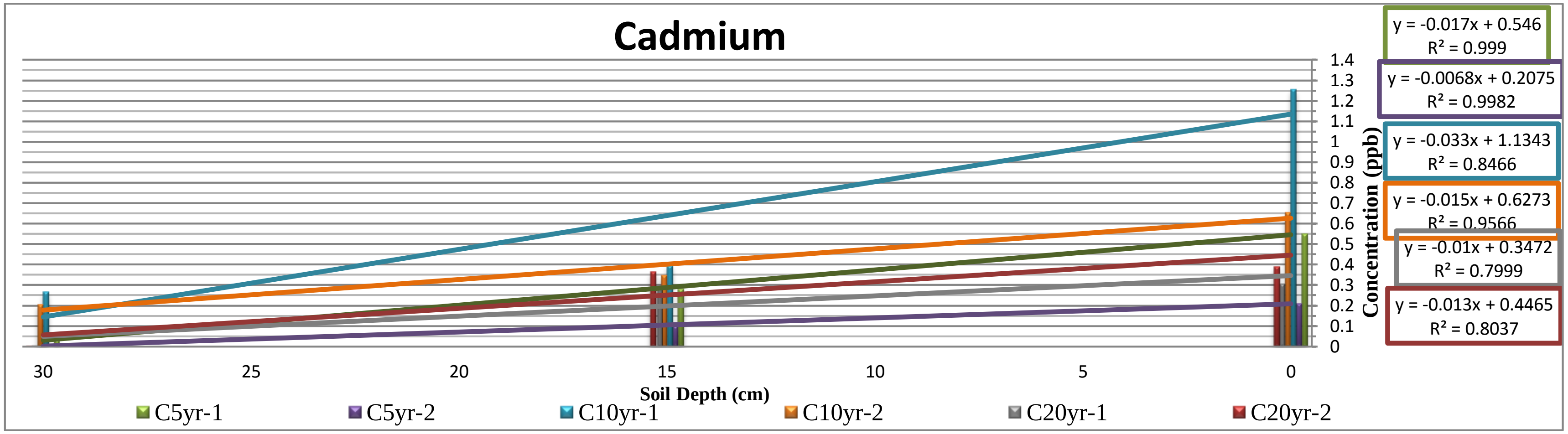


Figure 5.21: The Accumulation of Nickel and Copper in Different Soil Layers.



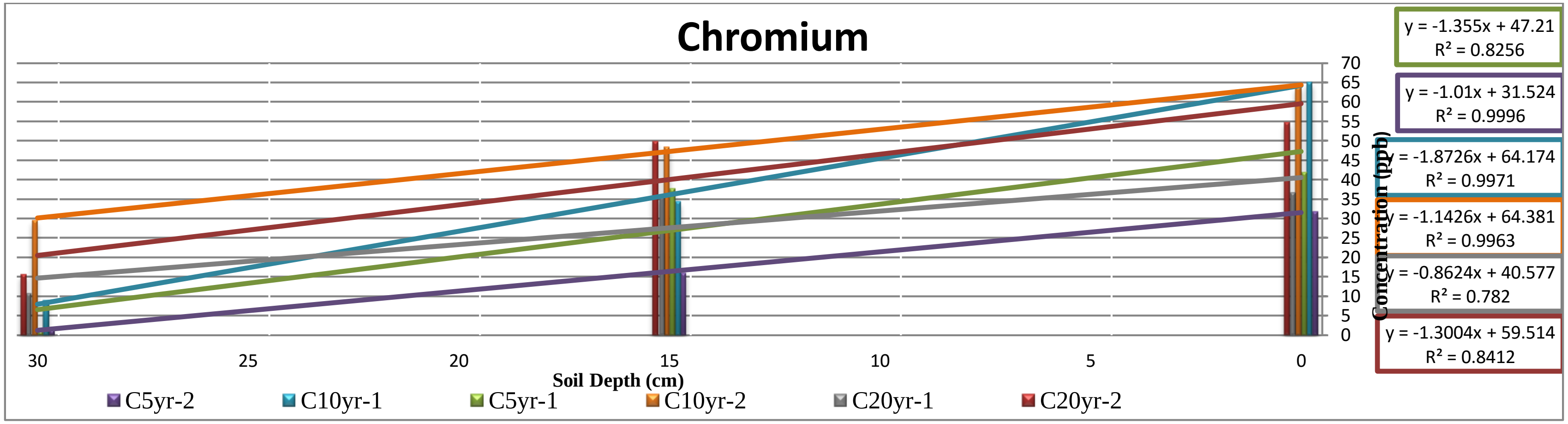


Figure 5.22: The Accumulation of Cadmium and Chromium in Different Soil Layers.

Chapter Six

Conclusions and Recommendations

Chapter Six

Conclusions and Recommendations

6.1 Conclusions

The following are the research main conclusions:

1- Wadi AlFaria stream, soil and groundwater wells Contain Ni, Cd, Cu and Cr at concentrations below the permissible limits.

2- The concentrations of Ni, Cd, Cu, and Cr in wet season are less than in the dry season.

3- In general, soil in Faria catchment has high adsorption capacity. The percentage of removed heavy metal by soil was high (between 80%-99%) for most of the selected heavy metals at different high inflow concentrations.

4- Small amounts of Ni, Cd, Cu and Cr were released with effluents at 5yr and 10yr concentrations. While in concentration of 20yr the release of heavy metals makes sense, since the relation becomes linear (R^2 value approaches to 1) and the change in concentration with time is constant and negative.

5- According to accumulation in soil profile layers; Ni, Cu, Cd, and Cr concentrations decrease when depth increases, and the depth-concentration relation is linear since R^2 values approach to 1, and all zero concentrations occurred at little depth from the surface.

6- The possibility of Ni, Cu, Cd and Cr to reach groundwater from the stream through soil is weak.

6.2 Recommendations

Based on the outcome of this research, the following can be recommended:

1- Nablus municipality should eliminate the discharging of untreated industrial and domestic wastewater effluents from the eastern side of the city to Wadi AlFaria stream, these effluents are responsible for the existence of heavy metals in the wadi, by constructing wastewater treatment plant.

2- Public education regarding in order to increase the awareness of farmers in Faria catchment by distributing leaflets about the adverse effects of fertilizers and pesticides on soil and ground water because they are containing heavy metals.

3- Additional studies should be conducted to know the factors and soil properties which affect the mobility of heavy metals in soil.

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Annexes

Annex A: The Concentrations of Ni, Cd, Cu and Cr in Dry and Wet Seasons in Wadi AlFaria Stream, Soil and Groundwater for the six Selected Locations(ppb).

Element	Location	Surface	Soil 0-10 cm	Soil 10-30 cm	Soil 30-50 cm	Groundwater
Dry Season						
Ni	18-18/039	10.38	42.35	45.75	31.23	11.84
	18-18/036	16.35	42.72	31.41	42.14	4.24
	18-18/031	7.45	52.01	59.16	42.73	17.46
	18-18/035	23.80	64.81	33.60	30.50	12.09
	18-18/027	9.24	40.29	62.49	83.69	15.50
	18-18/034	9.81	47.62	54.29	58.38	4.43
Cd	18-18/039	0.091	0.097	0.083	0.11	0.089
	18-18/036	0.097	0.552	1.21	0.799	0.109
	18-18/031	0.083	0.584	0.632	0.935	0.314
	18-18/035	0.11	0.899	0.657	0.674	0.10
	18-18/027	0.089	0.542	1.07	0.646	0.141
	18-18/034	0.105	0.446	0.749	0.753	0.071
Cu	18-18/039	4.13	70.62	100.57	37.05	6.92
	18-18/036	3.94	29.77	30.78	33.69	3.72
	18-18/031	2.28	29.69	28.21	26.29	2.1
	18-18/035	5.42	58.77	37.21	36.28	4.64
	18-18/027	3.71	31.62	47.72	44.75	5.78
	18-18/034	3.99	22.72	26.81	26.38	4.46
Cr	18-18/039	9.07	46.60	54.07	33.87	1.56
	18-18/036	13.41	66.81	50.04	63.56	3.78
	18-18/031	1.68	54.60	52.77	46.45	18.49
	18-18/035	19.31	61.24	42.08	36.84	9.73
	18-18/027	4.54	46.54	71.24	63.20	8.42
	18-18/034	7.00	57.44	34.59	18.23	2.66
Wet Season						
Ni	18-18/039	5.08	29.91	29.52	49.02	2.41
	18-18/036	4.90	34.51	32.14	42.27	2.17
	18-18/031	5.23	21.35	52.20	26.39	3.01
	18-18/035	5.24	49.27	49.90	45.76	2.49
	18-18/027	5.07	49.80	41.05	51.47	1.87
	18-18/034	4.87	10.69	41.40	43.77	2.12
Cd	18-18/039	0.045	0.672	1.125	1.294	0.059
	18-18/036	0.085	0.434	0.787	3.15	0.067
	18-18/031	0.071	0.737	0.304	0.543	0.043
	18-18/035	0.067	0.641	1.058	2.081	0.032
	18-18/027	0.025	0.44	1.284	0.982	0
	18-18/034	0.059	0.185	0.711	0.767	0.076
Cu	18-18/039	2.24	30.97	42.90	30.80	2.38
	18-18/036	2.33	24.65	32.24	44.53	1.93

	18-18/031	2.78	15.62	32.12	16.32	7.31
	18-18/035	2.07	47.73	24.27	43.65	5.89
	18-18/027	2.62	33.94	43.52	37.16	2.72
	18-18/034	2.50	10.94	50.24	20.07	3.60
Cr	18-18/039	5.09	30.92	30.43	48.43	3.86
	18-18/036	5.66	39.31	33.12	42.97	5.19
	18-18/031	8.39	12.47	57.66	17.40	5.08
	18-18/035	6.22	58.72	57.32	45.57	4.31
	18-18/027	8.17	56.79	43.81	59.47	6.39
	18-18/034	5.77	14.76	43.92	38.21	4.16

Annex B: Soil Sampling Location for Column Study Experiment

Annex C: Outflow Results of the Column Study Experiment (ppb).

5 yr-1							
Element	**0**	**4**	**8**	**12**	**16**	**20**	**24**
Cd	0.13	0.172	0.19	0.11	0.089	0.103	0.054
Cr	20.72	20.05	10.99	13.68	15.30	11.87	12.18
Cu	21.81	16.37	18.07	9.36	9.91	12.56	8.88
Ni	23.59	16.01	23.90	15.57	16.28	15.79	13.86
5 yr-2							
Cd	0.123	0.198	0.014	0.04	0.01	0.01	0.06
Cr	16.11	18.28	10.12	7.76	13.41	5.92	7.18
Cu	20.20	20.92	10.84	12.00	5.37	4.83	7.64
Ni	18.34	24.23	11.51	8.84	8.43	6.75	11.59
10 yr-1							
Cd	0.177	0.149	0.021	0.019	0.051	0.051	0.07
Cr	24.63	19.16	11.60	9.27	13.76	13.13	12.02
Cu	19.23	17.57	9.82	7.93	9.29	7.94	8.94
Ni	21.22	21.82	10.93	10.55	15.67	14.95	14.83
10 yr-2							
Cd	0.12	0.06	0.03	0.04	0.05	0.06	0.09
Cr	19.09	13.67	3.46	9.09	7.43	11.48	7.09
Cu	12.07	3.41	2.19	5.90	3.66	6.43	2.21
Ni	21.75	4.18	3.95	10.36	8.46	15.35	6.93
20 yr-1							
Cd	0.219	0.156	0.156	0.116	0.147	0.098	0.03
Cr	37.44	35.29	34.05	24.70	27.20	14.99	11.07
Cu	18.548	18.514	17.231	14.785	14.553	14.636	8.615
Ni	42.646	34.5	41.06	28.139	30.983	17.08	16.025
20 yr-2							
Cd	0.226	0.186	0.075	0.096	0.089	0.033	0.024
Cr	39.72	23.99	30.30	16.85	17.87	13.62	3.57
Cu	27.09	21.25	15.98	16.76	16.2	7.24	7.15
Ni	36.13	27.32	15.15	22.61	20.35	8.68	4.06

Annex D: Soil Profile Results of the Column Experiment (ppb).

5 yr-1			
Element	**Top**	**Medium**	**Bottom**
Cd	0.55	0.282	0.033
Cr	1.167	37.672	41.816
Cu	0.858	12.093	14.736
Ni	0.048	26.991	28.771
5 yr-2			
Cd	0.1	0.21	0.005
Cr	1.391	31.69	16.041
Cu	0.766	9.884	4.39
Ni	0.311	20.445	10.451
10 yr-1			
Cd	0.266	0.7	0.396
Cr	8.878	34.322	65.056
Cu	1.754	14.211	18.833
Ni	5.351	26.132	43.679
10 yr-2			
Cd	0.205	0.655	0.347
Cr	29.5	63.777	48.451
Cu	12.675	20.679	14.738
Ni	32.078	53.443	37.551
20 yr-1			
Cd	0.284	0.284	0.005
Cr	10.761	36.633	35.528
Cu	1.074	15.401	10.576
Ni	4.649	28.575	28.625
20 yr-2			
Cd	0.363	0.391	0.002
Cr	15.608	49.793	54.621
Cu	0.603	19.207	18.258
Ni	4.186	36.318	43.724

جامعة النجاح الوطنية

كلية الدراسات العليا

تقييم انتقال المعادن الثقيلة من وادي الفارعة الى التربة و المياه الجوفية

إعداد

أمامة منذر حسني الرفاعي

إشراف

أ.د . مروان حداد

د . ماثر صوالحة

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في هندسة المياه والبيئة في كلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2015

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الملخص

حوض الفارعة هي واحدة من أهم المناطق في الضفة الغربية في فلسطين, نظرا لكثافة النشاطات الزراعية فيها, حيث أنها تحتوي على العديد من الآبار الجوفية والينابيع التي تستخدم لري المزروعات بالإضافة إلى الاستهلاك المنزلي. لذا نوعية وجودة مصدر المياه الجوفية يعتبر قضية مهمة. المعادن الثقيلة هي واحدة من أكثر الملوثات سمية التي يجب أخذها بعين الاعتبار. لذا فان الهدف من هذه الدراسة هو تقييم تركيز كل من النيكل والكادميوم والنحاس والكروميوم في مياه وادي الفارعة والتربة والمياه الجوفية من ستة مواقع تم اختيارها من المنطقة. ثم سيتم مقارنة هذه التراكيز بالحد الأقصى المسموح به في مياه الري والتربة. الهدف الثاني هو نمذجة انتقال هذه المعادن الثقيلة باستخدام تجربة عمود التربة.حيث تم استخدام عمودين لتمثيل التراكيز لمدة 5 سنوات, عمودين لتمثيل التراكيز لمدة 10 سنوات, عمودين لتمثيل التراكيز لمدة 20 سنة. وذلك للتعرف على مصير هذه المعادن المختارة في التربة وفيما إذا كان هناك احتمالية لوصولها إلى المياه الجوفية وتلويثها في منطقة الفارعة.

النتائج تشير إلى وجود كل من النيكل والكادميوم والنحاس والكروميوم في مياه الوادي والتربة والمياه الجوفية في الستة مواقع المختارة من منطقة الفارعة بتراكيز اقل من الحد المسموح به للتربة ومياه الري. وان التراكيز في فصل الجفاف كانت اكبر منها في فصل الرطوبة.

ايضا تم تحليل تراكيز المعادن الثقيلة (النيكل, الكاديميوم, النحاس والكروميوم) باستخدام الانوفا حيث تبين انه لا يوجد تغير في التراكيز بين المواقع الستة المأخوذة منها العينات.

بالنسبة لتجربة عمود التربة, النتائج توضح ان تركيز المعادن الثقيلة المختارة في الماء المتدفق من العمود قليل جدا ومتناقص مع الزمن خلال فترة التجربة والتي كانت 24 ساعة. وعلى المدى البعيد العلاقة بين التركيز والوقت تقترب من ان تصبح علاقة خطية كما يتضح من نتائج الأعمدة التي تحمل التراكيز لمدة 20 سنة. معظم كميات النيكل والنحاس والكروميوم تراكمت في النصف الأول الثاني من عمود التربة. بالاعتماد على قيمة الجذر التربيعي R^2فان العلاقة بين التركيز وارتفاع عمود التربة هي علاقة خطية حيث كلما زاد العمق في عمود التربة قلت تراكيز المعادن الثقيلة المختارة. وعليه تم حساب العمق الذي تكون التراكيز عنده تساوي صفر وكانت الاعماق كالاتي: 32.97,سم ,48.10سم ,38.50سم في الأعمدة التي تمثل التراكيز لمدة 5 سنوات, 10 سنوات و20 سنة على التوالي. مما يعني أن التربة متجانسة وقادرة على ادمصاص المعادن الثقيلة.

بشكل عام التربة في منطقة الفارعة تمتلك سعة ادمصاص عالية للمعادن الثقيلة المختارة على مختلف التراكيز العالية. ولكن وجود هذه المعادن الثقيلة في عينات المياه الجوفية يعنى انه تم انتقالها من مياه الوادي وادمصاصها بواسطة التربة حتى وصلت إلى آبار المياه الجوفية, حتى ولو كانت بتراكيز قليلة. هذا يشير الى وجود مخاطر محتملة لتلوث المياه الجوفية بالمعادن الثقيلة على المدى البعيدِ.