An-Najah National University

Faculty of Graduate Studies

Environmental Risk Assessment and modeling Heavy Metals Uptake by Barely irrigated with water containing heavy metals

By

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

2017

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Dedication

To My Father "Majed"

For earning an honest living for us and for supporting and encouraging me to believe in myself.

To My Mother "Fatina"

A strong and gentle soul who taught me to trust in Allah, believe in hard work and that so much could be done with little.

To My husband "Wajdy"

For your patience, love and friendship

For being the greatest man in the world in every way.

To My Sisters

"Wiam, Aseel, Hiba Allah, Raheeq and Mayar"

I am really grateful to all of you, you have been my imspiration and my soul mates.

To my happiness" little prince Omar".

To my Lovely Second Family “Uncle Omar, Aunt Fatima, Marah, Sekqi, Aseel, Gaith, Qais and Kenan"

To My Best Friends “Fatima, Samar, Shatha and Wal’a”

Acknowledgment

The completion of this undertaking could not have been possible without the participation and assistance of so many people whose names may not all be enumerated. Their contributions are sincerely appreciated and gratefully acknowledged.

However, I would like to express my deep appreciation and indebtedness particularly to the following:

My parents, my husband as well as, my sisters my family and my friends with love and respect.

I am so grateful to my supervisors Dr. Munqez Shtayah and Prof. Dr. Marwan Haddad, for their helpful efforts, fruitful guidance and continual encouragement through entire research.

I would like to thank the DFG for the financial support.

Doa'A Nassar

الإقرار

أنا الموقع أدناه، مقدم الرسالة التي تحمل العنوان:

Environmental Risk Assessment and modeling Heavy Metals Uptake by Barely irrigated with water containing heavy metals

أقر بأن ما شملته هذه الرسالة إنّما هو نتاج جهدي الخاص، باستثناء ما تمّت الإشارة إليه حيثما ورد، وأنّ هذه الرسالة ككل، أو أيّ جزء منها لم يقدّم من قبل لنيل أيّ درجة أو لقب علميّ لدى أيّ 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 الطالب:**

Signature: **التوقيع:**

Date **التاريخ**

Table of Content

List of Tables

Table of Figures

List of abbreviations

ANOVA	Analysis Of Variance
AUS. EPA	Australian Environmental Protection Agency
FAO	Food and Agriculture Organization
GLM	Generalized Linear Model
ICP- MS	Inductively Coupled Plasma Mass Spectrometry
PS	Palestinian Standards
US. EPA	United States Environmental Protection Agency
WHO	World and Health Organization

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Abstract

This experiment was implemented in order to study the effect of the irrigation of simulated treated wastewater on soil, shoots and roots of barely and to mitigate the risk resulting from this irrigation, if any. The experiment was conducted under controlled conditions in the greenhouse at the Faculty of Agriculture and Veterinary Medicine, An-Najah National University, Tulkarm (Khadouri) during growing season (2013/2014). The barely was cultivated in plastic pots (6x6x7 cm) filled with agricultural sand in three blocks. The plants were irrigated using tap water, water simulated to the effluent of water treatment plant, water simulated to the effluent of water treatment plant after 3 years, after 9 years and after 15 years with three replicates for each treatment. Height of the shoot and number of leaves were monitored during the season. Chemical analysis was used for determining the heavy metals content (Cd, Cu, Cr, Fe, K, Mn, Ni, Pb, Zn) in each part of the plant (soil, shoots and roots) using the ICP-MS and these tests was conducted at An Najah National University (Water and Environmental studies institution laboratories). The collected data were analyzed using one way analysis of variance. Means were separated using the Duncan's multiple range test with $P \leq .05$, and the linear regression analysis. Risk assessment

was performed using AS/NZS ISO 31000: 2009 Risk Management – Principles and Guidelines. Enrichment factor, bio concentration factor and translocation factor were calculated. Results showed that the water type had no effect on the plant height in all treatments, whereas it affected the number of leaves, they decreased with time. Barely irrigated with the simulated treated wastewater showed a significant difference except for Zn. Cd, Cu, K and Mn have the highest concentration in plants, on the other hand, the remaining metals have higher content absorbed by soil. When comparing metal content in shoots, roots and soil with world health organization (WHO) thresholds in each, Cd, Fe, Pb and Zn were higher than the permitted levels in shoots, also Cd, Fe and Pb were higher than the permitted levels in roots. Whereas all the metals had lower content than the permitted levels of WHO in soil. When using the linear regression analysis, the p- value was > 0.05 in all models except for Chromium in plant. Enrichment factor, bio concentration factor and translocation factor have been calculated. From that, almost the values were > 1 indicating that the larger contents of heavy metals were in the plant.

In conclusion, the crop and soil quality parameters were significantly affected by long term irrigation with the treated wastewater, and this continuous treatment may lead to accumulation beyond the thresholds set by WHO. It should be noted that these results were observed using the simulated treated waste water over the years without taking into consideration the leachate property.

In addition the barely can be used for the phaytoextraction process for some metals (Cd, Cu, K, Mn and Zn). The treated waste water could not be used as an alternative to the fresh water for irrigating the barely.

Chapter One

General Introduction

Chapter One

1 General Introduction

1.1 General Background

Water is a vital resource but a severely limited one in most countries of the Mediterranean region including Palestine (Rusan et al., 2007). There is a gradual decline in availability of fresh water in Palestine according to the population increase and because the lack of control over the Palestinian water resources, and also to the adverse impact of the climate change (Abu Zahra, 2001).

At present, the average per capita water consumption by the Palestinian population is approximately 55 l/c/d, or 55% of the world health organization (WHO) minimum standard of 100 l/c/d. This is shows that water supply for the Palestinian population is inadequate according to the international standards (Abu Zahra, 2001). In order to deal with this shortage, the idea of generating new water resources appeared, such as: treatment, sanitation … etc (Abdel-Kader, 2013).

Many countries are struggling to balance water distribution among municipal, industrial, agricultural, and recreational uses. The population growth not only increased the fresh water demand but also increased the volume of wastewater generated. Treated or recycled wastewater appears to be the only water resource that is increasing as other sources are decreasing. Treated water is increasingly viewed as a valuable resource for the agricultural, industrial and municipal sectors, rather than as a waste that requires disposal (Darvishi et al., 2010).

Palestine is located in the transitional zone between the arid desert climate of the Sinai Peninsula and the temperate and the semi humid Mediterranean climate. It is one of the places where the exploitation level of recourses exceeds the capacity of the environment. This is especially true for the water and land resources, which are under high pressure and subject to sever over exploitation, pollution and degradation. The scarcity of water in the Mediterranean and Middle East countries requires endorsement of sustainable wastewater management. The wastewater related problems, which these countries are facing, are increasing yearly owing to the increasing discharge of wastewater as a result of the increasing demand of fresh water for industrial purposes, human consumption and agricultural productions.

Since wastewater is considered as a non-ordinary source of water, its usage in agriculture demands a unique management, which in addition to its appropriate utilization, has to have no threat to the environment, plants, soils and surface and subsurface water resources (Abu Nada, 2009). Most technologies focus on the treatment in order to face the water shortage and to reduce the pressure on the limited water resources (Hamaiedeh, 2010). The use of treated municipal wastewater in countries poor in water resources is less expensive and considered an attractive source of irrigation. (Rusan et al., 2007). Irrigation with treated municipal wastewater is considered an environmentally sound wastewater disposal practice compared to its direct disposal to the surface or ground water bodies (Rusan et al., 2007).

Greywater is wastewater originating from showers, baths, bathroom sinks, kitchen sinks and laundries. It does not include toilet or garbage wastes, or wastewater contaminated by soiled diapers (Shamabadia et al., 2015). Greywater is often combined with black water in a single domestic wastewater stream. Yet greywater can be of higher quality than black water because of its low level of contamination and higher potential for reuse. In particular, the reuse of greywater can help reduce demand of fresh water (Allen et al., 2010). The use of grey wastewater for irrigation has been recorded in Germany and United Kingdom (UK) in the 16th and 18th centuries respectively. Irrigation with grey waste and other waste water also has a long history in China and India (Chiroma et al., 2014).

In general grey wastewater contains lower levels of organic matter and nutrients compared to wastewater, the levels of heavy metals are however in the same concentration range (Eriksson et al., 2002). The grey wastewater is considered not only a rich source of organic matter and other nutrients but also harbors heavy metals like Fe, Mn, Cu, Zn, Pb, Cr, Ni, Cd and Co at high concentrations in receiving soils (Chiroma et al., 2014).

Heavy metals are poisonous metals having density five times greater than water (6.0 g/cm^3 or more). They are toxic for all living organisms and they are the main source of pollution in the environment. They enter into the human body through many ways like ingestion and absorption. They become harmful when their accumulation rate is more than their discharge rate. They accumulate slowly in the body over a long time and they are toxic (Sardar et al., 2013). Several methods were used to clean the environment from heavy metals but most of these methods are costly and difficult (Tangahu et al., 2011). There are 23 heavy metals available in nature such as Cadmium (Cd), Copper (Cu) and Arsenic (As).

Human activity like industries, mining, waste disposal, domestic and industrial effluents, vehicle exhausts, pesticides and fertilizers lead to increasing levels of heavy metal contamination in the environment (Tüzen, 2003). Unlike organic pollutants, heavy metals do not biodegrade and are usually not mobile, and the soil acts as a long-term sink for heavy metals (Pourang and Noori, 2014).

The attention to the concentrations of heavy metals in agricultural soils is increasing because of food safety and human health, due to their carcinogenic effects (Bigdeli and Seilsepour, 2008). Immoderate accumulation of trace metals in agricultural soils through wastewater irrigation may do not only cause an accumulation in the soil but also leads to high plant uptake from these heavy metals. In addition, there is also a chance for transferring these metals into the environment, especially groundwater systems through leaching (Pourang and Noori, 2014).

Barley (*Hordeum vulgare* ssp. *vulgare*) is among the world’s earliest domesticated and most important crop plants, and it represents the fourth most plentiful cereal (Badr et al., 2000). It was one of the earliest widespread crops in the Middle East. It’s important due to it is historical and religious background and also to its medical importance (Badr et al., 2000). Barley grain is a mostly used as a feed for animals, malt and food for human consumption. Also, its' grain is a good source of animal feed. The Global Barley production distributed as: 75% for animal feed, 20% is malted for use in alcoholic and non-alcoholic drinks, and 5% as a food products. Barley is widely acclimatized for diverse environmental conditions and is more stress tolerant than wheat (Begna et al., 2014).

1.2 Study Justifications

Depletion of water resources and deterioration of water quality in both West Bank and Gaza are very important environmental themes that require direct and urgent measures. Groundwater resources are rapidly deteriorating by infiltration of untreated wastewater, influencing directly the quality and availability of this scarce and essential resource. (Fatta et al., 2004).

The situation of the sewerage system is extremely critical. Both the West Bank and Gaza are facing a series of wastewater and sanitation related problems. These are: large scale discharge of untreated wastewater, leaking of collected wastewater from sewer systems and cesspits, water treatment plants that are badly functioning and uncontrolled reuse of untreated waste water by irrigation sector (Fatta et al., 2004).

Generally, there is a major potential use of recycled water in Palestine. It is, however, essential that the development of water reuse in agriculture be based on scientific evidence of its effects on environment (soil and crops). Despite meeting the regulations and guidelines, the reuse of wastewater is not entirely risk-free. Continued research will result in developing new technologies or improving the existent methodologies used for assessment of risk associated with trace contaminants, evaluation of microbial quality, treatment systems, and evaluation of the fate of microbial, chemical and organic contaminants (Abu Nada, 2009). This reflects the need to analyze and evaluate the effects that will arise from wastewater agriculture use of specific reuse projects. Moreover, while many wastewater reuse projects have been practiced in Palestine, none of them have a comprehensive long term impact analysis on soil and crop. This study will carry out these analysis based on actual field analysis.

1.3 Research questions

1. Do heavy metals accumulate in soil over years? If so, at what levels they will accumulate?
2. Do barley plants absorb heavy metals? If so, to what level they will accumulate in roots and shoots?
3. What is the rate of the absorption?
4. Do these accumulations cause a risk to the environment according to WHO standards?

1.4 Research Objectives

Studying Barley's absorption of heavy metals is important to protect the natural life, protect the plants, soil, animals and people's lives, and protect the public health.

Cultivation of Barley in the incubator in specific conditions was used to simulate the reality in order to analyze and find the absorption.

Specifically, the following tasks will be analyzed and discussed in the thesis:

1. To assess the effects of long-term irrigation with sewage effluents on metal contents in soils and plants.
2. To assess the environmental risk of these heavy metals.

1.5 Research Motivations

In Palestine, the concentrations of heavy metals are continue to increase over the years, because of the development of different industries. And it is inevitable, even at low concentrations, there is a risk on the environment. So the outcome of this research is with great importance to the decision makers. The main objective of this study is to investigate the agronomic impact of treated wastewater reuse on the soil and on forage crops (Barley) when it is irrigated using simulated treated effluent for long-term (Fifteen years). As an approach to achieve the objectives, analyses of plant, root and soil was presented and discussed. Moreover, the national and international reuse guidelines were reviewed and compared with this case. Finally, regional and international experiences are highlighted to bridge the gap between the farmers and the researchers in the confidence of using the treated effluent for irrigation purposes.

Chapter Two
Literature Review

Chapter Two

2 Literature Review

2.1 Heavy metals

Over the years, the researches choose to discuss the importance of the heavy metals. The effect of these metals not limited to water; they also strongly affect soil, plants, animals and humans. This is apart from being a devastating the public health.

Agriculture is the main source of income in the countries that have a water shortage or water scarcity. The need to use the domestic and industrial wastewater for the irrigation of the crops arises to be a lucrative option, these waste waters contain appreciable amounts of heavy metals (Rattan et al., 2005).

The concentrations of heavy metals in sewage effluents are usually low, but long-term use of these wastewaters on agricultural lands often results in the buildup of elevated levels of metals in soils (Lu et al., 2015).

Toxicity of heavy metal depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals (Tchounwou et al., 2012).

Heavy metal pollution is seriously problematic because it is persistent, difficult to detect, and remediate (Bao et al., 2014). They contribute to environmental pollution because of their unique properties, mainly that they are non-biodegradable, non-thermo-degradable and generally do not leach from the topsoil (Mapanda et al., 2005).

They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer (Tchounwou et al., 2012).

However, each metal is known to have unique features and physic-chemical properties that confer to its specific toxicological mechanisms of action (Tchounwou et al., 2012).

Cadmium is a mobile element, easily absorbed by roots and transported to shoots. It is uniformly distributed in plant organs. Cadmium (Cd) presents an increasing international concern because it is very persistent in the environment, extremely toxic to plants and animals and is easily absorbed by plants and transported to upper parts, thus presents a risk for consumers (Gvozdena et al., 2013). It is recognized as an extremely significant pollutant due to its high toxicity and large solubility in water (Gubrelay et al., 2013). Cadmium compounds are used in electric batteries, electronic components and nuclear reactors. Cadmium concentrations in unpolluted natural waters are usually below 1 µg/l (WHO, 2011).

Contamination of drinking-water may occur as a result of the presence of cadmium as an impurity in the zinc of galvanized pipes or cadmium-containing solders in fittings, water heaters, water coolers and taps. Both kidney and liver act as cadmium stores; 50–85% of the body burden is stored in kidney and liver, 30–60% being stored in the kidney alone. Because of the considerable age-related accumulation of cadmium in the body, only a small part of the cadmium absorbed will be excreted in the urine (WHO, 2011).

Another metal is Chromium. It is a naturally occurring element present in the earth's crust, with oxidation states (or valence states) ranging from chromium (II) to chromium (VI) (Tchounwou et al., 2012).

Chromium and its salts are used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry, and in photography (WHO (1), 1996). The health hazard associated with exposure to chromium depends on its oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form (Tchounwou et al., 2012).

Zinc (Zn) is one of the important trace elements that plays a vital role in the physiological and metabolic process of many organisms. Nevertheless, higher concentrations of zinc can be toxic to the organism. It is a metal which shows fairly low concentration in surface water due to its restricted mobility from the place of rock weathering or from the natural sources (Nazir et al., 2015). Zinc occurs in small amounts in almost all igneous rocks. Zinc is used in the production of corrosion-resistant alloys and brass, and for galvanizing steel and iron products. In tap water, zinc concentration can be much higher as a result of the leaching of zinc from piping and fittings (WHO (2), 1996).

Lead (Pb), it is a toxic metal that is harmful to human health; there is no safe level for lead exposure. The primary source for lead in most drinking water sources is the piping used within a distribution system or the household pluming. Other routes of lead exposure include: lead paint used in homes prior to 1978, dust or soil containing lead, food grown in contaminated soil or stored in poorly glazed pottery, and more (Tong et al., 2000). Lead as a soil contaminant is a widespread issue; it accumulates with age in bones, aorta kidney, liver and spleen. The greatest percentage of lead is taken into the kidney, followed by the liver and the other soft tissues such as heart and brain (Tchounwou et al., 2012). It can enter the human body through uptake of food (65%), water (20%) and air (15%) (Nazir et al., 2015).

Copper (Cu) is a reddish metal that occurs naturally in rock, soil, water, sediment, and air. Also, it is found in surface water, groundwater, seawater and drinking-water. Copper is used to make electrical wiring, pipes, valves, fittings, coins, cooking utensils and building materials. It is present in munitions, alloys (brass, bronze) and coatings (WHO, 2004). Some people who drink water containing copper in excess of the action level over many years could suffer liver or kidney damage (Minnesota Department of Health, 2008).

Other heavy metals are iron (Fe) and manganese (Mn), they are nonhazardous elements that can be nuisance in water supply, but they can cause offensive taste, appearance and staining. They are similar metals. Of the two, iron is found most frequently in water. Manganese is often found in waters that contain iron (Dvorak and Skipton, 2014). Iron and manganese are common elements in the earth’s crust. As water percolates through soil and rock it can dissolve these minerals and carry them into groundwater. And they are not considered health hazards (Dvorak and Skipton, 2014).

Nickel (Ni) is a chemical element and abundant on Earth. Nickel easily forms nickel-containing alloys, which have found an ever increasing use in modern technologies for over a hundred years now (Duda-Chodak and Blaszczyk, 2008). During the last decades, Ni has become a serious concern as its concentration has reached up to 26,000 ppm in polluted soils. Ni, in contrast to other toxic trace (heavy) metals like cadmium, lead, mercury, copper and chromium, has received little attention from plant scientists due to its dual character and complex electronic chemistry which is a major hurdle in disclosing its toxicity mechanism in plants (Syam et al., 2016).

In water, Ni derives from biological cycles and solubilization of nickel compounds from soils, as well as from the sedimentation of nickel from the atmosphere. Uncontaminated water usually contain about 300 ng Ni.dm^{-3}. Farm soils contain approximately 3-1000 mg Ni.kg^{-1} soil (Duda-Chodak and Blaszczyk, 2008).

Potassium (K) is one of the seven essential macro minerals, along with calcium, magnesium, phosphorus, sodium, chloride and sulfur. Potassium is a very important mineral for the proper function of all cells, tissues, and organs in the human body (Ehrlich, 2015). Potassium's primary functions in the body include regulating fluid balance and controlling the electrical activity of the heart and other muscles. Potassium helps to maintain a healthy blood pressure to support (Ehrlich, 2015). The World Health Organization recommends an intake of 3,510 mg per day and agrees that most of the world's population is not meeting this recommendation (WHO, 2012).

We ingest these heavy metals every day, in the food we eat, in the air that we breathe and in the water that we drink, Some metals, the essential minerals, such as zinc (Zn), iron (Fe), copper (Cu), manganese (Mn) and magnesium (Mg), we need to ingest since they are required for normal growth and survival, while other metals such as cadmium (Cd), lead (Pb) and mercury (Hg) are only harmful to living systems.

In a study on heavy metals made over 10 years on agricultural soil. In China (Wei and Yang, 2010), the concentrations of Cr, Ni, Cu, Pb, Zn, As, Hg and Cd were higher than their background values, Among the cities, the contamination levels of the heavy metals vary in a large range. Generally, this study also found that the contamination levels of Cu, Pb, Zn and Cd are higher than that of Ni and Cr.

Not only the plant could be affected by the heavy metals, but also the soil and the ground water. In conventional wastewater treatment, considerable portions of heavy metals remain in the treated effluent if special advanced treatment is not conducted. Thus, long term effects of irrigation with wastewater might include pollution of ground water and soil with heavy metals such as Pb, Cu and Zn ions. A study in Palestine on samples taken from two sites (AL-Subu et al., 2003) showed that the concentrations of heavy metals were relatively high and there is availability to contaminate the ground water. The study recommended to separate the industrial waste water from the domestic or at least treat them before spilling them into the domestic waste water.

As the heavy metals can’t be devastated or be metabolized by any living organism, they accumulate in plants and humans in addition to the soil. When the soil is contaminated by heavy metals, this will adversely affects the whole ecosystem. Heavy metals are toxic to plants, animals, and human beings when the contaminated soils are used for crop production. There are also studies showed that the absorption and the accumulation of heavy metals in crop plants differs in different parts and that there is a broad difference in metal uptake between plant species and even between cultivars of the same plant species (Satpathy et al., 2014).

2.2 Treated waste water

The Long-term use of these waste waters in agriculture can cause an excessive accumulation of heavy metals in soil. These elevated quantities of heavy metals can cause clinical problems to animals and human beings which consume these plants rich of heavy metals. And because the food chain is the main route for entering the heavy metals into the bodies, monitoring the metals in the contaminated soils has generated a lot of interest (Rattan et al., 2005).

Due to water scarcity and the population expansion at a high rate then the need for increasing food productivity and the need for other water sources increase. Treating waste water is one solution.

Wastewater contains inorganic substances from domestic sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc, etc. Even if toxic materials are not present in concentrations likely to affect humans, they might well be at phytotoxic levels, which would limit their agricultural use (Pescod, 1992).

The use of treated wastewater as an irrigation source become widespread. An experiment was conducted on various cereals, millet, vegetables and fodder crops planted using both ground water and wastewater. Soil, plant, sewage effluent and ground water samples were taken and analyzed to find out that sewage effluents contained much higher amount of P, K, S, Zn, Cu, Fe, Mn and Ni compared to groundwater. Risk assessment in respect of metal contents in some vegetable crops grown on sewage - irrigated soil indicated that these vegetables be safely consumed by human (Rattan et al., 2005).

In Zimbabwe, the use of treated wastewater in urban horticulture made a socio economic benefits, but it also had bad environmental and health impacts such as land degradation. Soil samples were analyzed and the results indicated that the use of wastewater in urban horticulture enriched soils with heavy metals to concentrations that may pose potential environmental and health risks on the long-term (Mapanda et al., 2005).

2.3 Wastewater Reuse in Palestine

Years of neglect during the occupation from 1967 to 1994 have created severe environmental problems in West Bank and Gaza. Lack of wastewater treatment plants, of sewerage systems and of wastewater collection for recycling lead to the uncontrolled discharge of wastewater into the environment. Eighty-eight percent of households are connected to a water supply network, while only 45% of households are connected to a sewage collection system (PCBS, 2007). About 31 million cubic meters (MCM) of wastewater is collected per year, and 75% is discharged directly into the environment without any treatment due to a lack of functioning treatment plants (Fatta et al., 2004). Proper treatment of wastewater is challenging due to limited funding, lack of infrastructure, and the depressed economy. The situation is further complicated by the ongoing Israeli occupation (McNeill et al., 2008). Raw wastewater in the major West Bank cities found biochemical oxygen demands (BOD) of 500–1000 mg/L, chemical oxygen demands (COD) of 1000–3000 mg/L, and total nitrogen of 70– 280 mg/L (Birzeit University 2004).

There are five major wastewater treatment plants, thirteen small wastewater treatment plants and more than 700 on site small scale wastewater treatment plants.

Table 1: Treatment plants in West Bank

Treatment plant	Flow
Nablus West plant	15,000 m3/day
Jenin plant	14,000 m3/day
Al-Bireh plant	5,750 m3/day
Ramallah plant	1,500 m3/day
Tulkarem pretreatment plant.	15,000 m3/day

Table 2: Treatment plant parameter

Treatment Plant	Parameter	Actual average value(mg\l)	Standard value(mg\l)
Nablus	COD inlet flow	1315	1100
	COD outlet	315	100
	Outlet BOD_5	140	20
	Total suspended solids (TSS)	256	30
Al-Birah	COD inlet flow	1315	1100
	COD outlet	315	100
	Outlet BOD_5	140	20
	Total suspended solids (TSS)	256	30
Ramallah	COD inlet flow	853	1100
	COD outlet	89	100
	Outlet BOD_5	6	20
	Total suspended solids (TSS)	144	30

Jenin	COD inlet flow	1675	1100
	COD outlet	163	100
	Outlet BOD_5	290	20
	Total suspended solids (TSS)	617	30
Tulkarm	COD inlet flow	1152	1100
	COD outlet	502	100
	Outlet BOD_5	282	20
	Total suspended solids (TSS)	326	30

(Source: Joudeh et al., 2015)

2.4 Mobility of heavy metals in soil

Industrial activities have a very negative impact on the environment, on the long term, dust and metals can migrate to soil, surface water and ground water. Heavy metals bioavailability is regulated by physical, chemical and biological processes and there interactions. It also depends on several soil properties which are including granulometric composition, organic matter content, pH value, sorption capacity, content of macro and micronutrients, oxidation-reduction potential, activity of microorganisms, bioavailability for plants and animals and resistance of the soil (FijaŁKowski et al., 2005).

According to granulometric composition in soil, it was observed that when the grain size decrease, the concentration of heavy metals increase. Because sandy soils consist of coarser grains and having small adsorption capacity, it has the lowest heavy metal content (Szabo and Czeller, 2009).

2.5 Barley production

Barley (*Hordeum vulgare*) is a widely grown and highly adaptable winter cereal crop that is used mainly for stock feed and the production of malt for the brewing industry. Barley is an annual plant that has been selected from wild grasses. It is thought to have been an important food crop from as early as 8000 BC in the Mediterranean/ Middle East region. Barley is mostly used for feed and fodder besides being a significant crop industrially, particularly in the manufacture of beer. Quality wise barley is multifaceted. It is a rich source of B vitamins and essential minerals. It is also rich in fiber content, particularly beta-glucan, which has many health benefits, like keeping the blood sugar levels low for benefit of diabetics and checking cholesterol deposition for safety against heart ailments. Although beta-glucan content may be high for food, it should be low for beer production (Fettell et al., 2010).

The area of land cultivated with field crops totaled 495.4 dunums in the Palestinian Territory during the 2007/2008 agricultural year, barley total cultived ares were 107,548 dunums and it is production equal to 9740 kg (PCBS, 2009). But in 2010/2011 agricultural year the area of land cultivated with field crops decreased to be 245,414 dunums in the Palestinian Territory: 220,882 dunums in the West Bank and 24,532 dunums in Gaza Strip. The largest cultivated area of field crops was in Hebron governorate with 25.4% while the smallest was in Jerusalem governorate with 0.4%. Rainfed field crops made up 230,815 dunums (94.1%) while irrigated field crops totaled 14,599 dunums. The total production of field crops in the Palestinian Territory was 44,404 metric ton: 36,521 metric ton in the West Bank and 7,883 metric ton in Gaza Strip (PCBS, 2012).

Area, Yield and Production of Field Crops in the Palestinian Territory by Crop and Type, 2007/2008

Crop	الإنتاج Production	المساحة الكلية Total Area	Irrigated مروي		Rainfed بعلي		المحصول
			Yield الإنتاجية	Area المساحة	Yield الإنتاجية	Area المساحة	
Wheat	31,826	229,441	300	3,200	136	226,241	قمح
Barley	9,740	107,548	300	990	89	106,558	شعير
Sern	8,953	27,488	40	109	327	27,379	بيقيا
Clover	9,212	22,601	742	1,227	388	21,374	برسيم
Potato	69,180	21,177	3,340	20,061	1,950	1,116	بطاطا
Dry Onion	40,054	17,326	3,730	5,653	1,625	11,673	بصل يابس
Vetch	873	16,190	-	-	54	16,190	كرسنة
Chick-peas	1,741	14,575	-	-	119	14,575	حمص
Lentil	436	11,395	-	-	38	11,395	عدس
Tobacco	333	4,372	-	-	76	4,372	تبغ
Broad bean	339	3,994	-	-	85	3,994	فول
Sesame	254	3,781	-	-	67	3,781	سمسم
Thyme	3,227	2,211	1,932	1,601	220	610	زعتر
Anise	141	2,137	-	-	66	2,137	يانسون
Sweet Potato	4,895	1,780	2,750	1,780	-	-	بطاطا حلوة
Dry Garlic	1,371	1,573	1,953	430	465	1,143	ثوم يابس
Others Clover, Sern	127	1,386	-	-	92	1,386	محاصيل بذور أخرى

Figure 1: Area and production of field crops in Palestine territory by crop and Type, year 2007/2008

2.6 Summary

Heavy metals are toxic substances, toxic to humans, animals and also to the environment when exceed the maximum allowable limits. Long term waste water irrigation may lead to the accumulation of heavy metals in agricultural soils and plants. Crops accumulate heavy metals in their parts, although some of the heavy metals such as Zn, Mn, Ni and Cu act as micro-nutrients at lower concentrations, they become toxic at higher concentrations. In the absence of water sources sustainability, treating waste water arises as a source of irrigation, therefore it is important to study its characteristics and the risks of the long term use irrigation.

This study differs from previous ones as it mainly deals with simulated treated wastewater effluent from wastewater treatment plants. The accumulation of heavy metals over fifteen years of wastewater were studied in the soil, shoots and roots of barely plants in light of international guidelines i.e. WHO, FAO.

Chapter Three
Methodology

Chapter Three

3 Methodology

3.1 Experimental setup

3.1.1 Experimental site

The experiment was conducted under controlled conditions in the greenhouse at the Faculty of Agriculture and Veterinary Medicine, An-Najah National University, Tulkarm (Khadouri), Palestine (32.31519º N, 35.02033º W) during growing seasons (2013/2014). Barely was sown at the 1st of November in plastic pots (6x6x7 cm) filled with agricultural sand in three complete randomized blocks. Agricultural sand was used in order not to stick with roots. As a result, the heavy metals that will be absorbed from the irrigated water will be conservative.

3.1.2 Plant material

The experiment was carried out using local barley landrace.

3.2 Irrigation

In this experiment, the planted seeds were irrigated two times a week, 50 ml each, until the spikes started to grow (till maturity). And during the growing season, number of leaves and plant height were recorded for each landrace at two week intervals.

3.3 Simulated treated wastewater preparation

The quality of irrigation water in this experiment was simulated to by equal to the quality of the water introduced from water treatment facilities in term of heavy metals.

Lead (Pb), Cadmium (Cd), Chrome (Cr), Zinc (Zn), Iron (Fe), Copper (Cu), Manganese (Mn), Nickel (Ni) and potassium (K) added in different concentration as showed in table 3.

Table 3: Simulated heavy metal concentration in irrigation water in ppm

Element	X	3X	9X	15X	Composition
K	15.0	45.0	135	225.0	KCl
Zn	0.1	0.3	0.9	1.5	Zn metal
Cu	0.2	0.6	1.8	3.0	$CuSO_4$
Fe	0.1	0.3	0.9	1.5	$FeCl_2$
Mn	0.02	0.06	0.18	0.3	$KMnO_4$

Ni	0.02	0.06	0.18	0.3	$NiCl_2$
Pb	0.02	0.06	0.18	0.3	Pb metal
Cd	0.02	0.06	0.18	0.3	Cd metal
Cr	0.02	0.06	0.18	0.3	Cr metal

1. The control (Tap Water).
2. X: that contained heavy metals concentration simulated to the effluent of water treatment plant.
3. 3X: that contained heavy metals concentration simulated to continuous irrigation with treatment plant effluent for three years.
4. 9X: that contained heavy metals concentration simulated to continuous irrigation with treatment plant effluent for nine years.
5. 15X: that contained heavy metals concentration simulated to continuous irrigation with treatment plant effluent for fifteen years.

3.4 Collecting Plant Samples-end of experiment

At maturity, samples were collected. Soil, shoots and roots were collected and stored separately in a small paper bag for chemical analysis.

3.5 Trace Elements Analysis

The concentrations of heavy metals were determined in each collected sample according to the following procedure.

3.5.1 Chemical Analysis

Chemical analysis was performed in the laboratory using ICP-MS (Inductively Coupled Plasma Mass Spectrometry) , which it is a type of mass spectrometry that is used to detect metals in a sample at concentrations as low as 1 part per trillion. The ICP-MS can be utilized as a quantitative tool to determine the concentration of a specific analyte, or as a qualitative tool to determine the metal speciation in a sample.

3.5.1.1 Plant and root

The procedure followed is from the "**Analysis of Major, Minor and Trace Elements in Plant Tissue Samples with ICP-OES and ICP-MS"** (University of Wisconsin – Madison, 2005)

a. **Procedure (before digestion):**

Samples were dried at 60 °C for two days and stored in a 5-gram vial or equivalent for airtight storage. Dry samples of weigh 0.50±0.01 g, or 1.0±0.02 g of wet sample. the samples was left for an hour in order to cool, when it becomes cooler and it can be handled, 5 mL of concentrated nitric acid [HNO_3 – 70 %] were added then samples at were soaked at room temperature for 2-3 hours.

b. **Procedure (Hot plate digester):**

Tubes were placed in the block heater and covered with plastic film to retard the water evaporation. Then, block heater was set at 70ºC (Keep heating at 70ºC for 3 days). The film cover was removed and properly disposed and the tubes were taken off the block heater. After that, 30% hydrogen peroxide was added at a ratio of 1 mL per sample. Tubes were placed back onto the block heater and they were heated for 20-30 minutes. Finally, all of the tubes were taken off the block heater and 50 mL mark. Then, they were left to sit for 30 minutes or more.

c. **Measurement by ICP-MS**

From the diluted sample 14 ml was taken and put in falcon tubes in order to be ready to find the final concentrations of heavy metals. Specifically, Lead Pb, Cadmium Cd, Chrome Cr, Zinc Zn, Iron Fe, Copper Cu, manganese Mn and Nickel Ni

3.5.1.2 Soil

The procedure followed is from the "**Analysis of Major, Minor and Trace Elements in Soil and Sediment Samples with ICP-OES and ICP-MS"** (University of Wisconsin – Madison, 2005).

a. **Procedure (before digestion):**

At First, samples were dried at 60 °C for two days, large stones/rocks or plant materials were removed. They were stored in a 5-gram vial or equivalent for airtight storage. Dry samples of weigh 0.50±0.01 g of the sample into 50-mL cleaned and air-dried digestion tubes (sandy samples: 1.00 gram). Drops of 20–30% (v/v) nitric acid were added to moisten the samples. Then, 5 mL of concentrated nitric acid were added to the samples.

b. **Procedure (Hot plate digester):**

All tubes were placed in the block heater and covered with plastic film to retard the water evaporation. Then, block heater was set at 70ºC for three days. Then, the film cover was removed and properly disposed.

Tubes were taken off the block heater and cooled for several minutes. After that, 30% hydrogen peroxide at a ratio of 1 mL per sample was added. Then, all tubes were placed back onto the block heater for 20-30 minutes. Finally, all tubes were taken off the block heater. After digestion, 5 ml of hydrofluoric acid [HF] (40%) were added and left for 24 hours. Then, water was added to the 50 mL mark and sit for 30 minutes or more. Finally the samples were mixed and Left overnight to let particles settle down after this digestion.

c. Measurement by ICP-MS

From the diluted sample 14 ml were taken and put in a falcon tubes in order to be ready to find the final concentrations of heavy metals. Specifically, Lead Pb, Cadmium Cd, Chrome Cr, Zinc Zn, Iron Fe, Copper Cu, manganese Mn and Nickel Ni.

3.5.2 Statistical analysis

Analysis of variance (ANOVA) was performed on field data (number of leaves and height of plant) and on laboratory data (concentrations of heavy metals) using GLM procedure of SAS STAT software, lsmeans were obtained and multiple comparisons among pairs were performed using the Duncan-test.

Linear regression was performed using SPSS software, version 21.

With respect to the Regression the model is

$$Y = a + bX$$

Where:

Y = the dependent variable.

X= the independent variable.

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

3.5.3 Factors

The metal enrichment factor (EF) is defined as the ratio of metal concentration in an organ of the plant grown on the contaminated soil and that in the organ of the plant grown on the uncontaminated soil (concentration of heavy metal in shoots / roots at specific treatment to the concentration of the same heavy metal in control). The metal bio concentration factor (BF) is defined as the ratio of the metal content in shoots and the total content in soil (concentration of the heavy metal in shoots / roots at specific treatment to the concentration of the same heavy metal in soil at the same treatment). The metal translocation factor (TF) is defined as the ratio between the metal content in shoots and that in roots (concentration of the heavy metal in shoots at specific treatment to the concentration of the same heavy metal in roots at the same treatment) (Brunetti et al., 2012).

3.5.4 Environmental Risk Assessment

Risk assessment is defined as the formal process of evaluating the consequence(s) of a hazard and their likelihoods/probabilities (Gormley et al., 2011).

Environmental Risk Assessment is a process for estimating the likelihood or probability of an adverse outcome or event due to pressures or changes in environmental conditions resulting from human activities, and it aims to assisting government agency staff in assessing and reporting environmental conditions.

Environmental Risk Assessment (ERA) is a flexible tool that can be applied:

- At a variety of scales and levels of detail appropriate to those scales
- For a variety of environmental issues
- At various levels of funding
- And for short, medium or long-term time scales.

The environmental risk assessment system that will be used is informed by AS/NZS ISO 31000: 2009 Risk Management – Principles and Guidelines (Council of standards New Zealand, 2009).

With relevant to this system, ERA approach involved:

1- Risk identification: is the process of determining risks that could potentially prevent the environment, enterprise, or investment from achieving the objectives.
2- Risk analysis: is the process of defining and analyzing the dangers to Environment caused by the experiment.
3- Risk evaluation: is the process used to compare the estimated risk against the given risk criteria so as to determine the significance of the risk.
4- Risk treatment: involves developing a range of options for mitigating the risk, assessing those options, and then preparing and implementing action plans.

5- Monitoring and review: a planned part of the risk management process and involve regular checking or surveillance. It can be periodic or ad hoc.

The risks that resulted from the long term irrigation of the Barely plant using simulate treated waste water containing heavy metals are:

1- The soil pollution that may leachate into ground water, which will effect on the public health.
2- The plant pollution, which also effect the public health.

After identifying the risks, the consequence and likelihood of each individual risk will be analyzed using the risk assessment matrix.

Table (4) and table (5) present the ratings for consequence and likelihood respectively.

Table 4: Ratings for the assessment of consequence levels

Consequence Level	Environment	Community
1	Low Level impact/s to land, biodiversity, ecosystem services, water resources or air.	Low-level social impact. Low level infringement of cultural heritage or minimal disturbance to heritage structures. Minimal impact on human rights
2	Minor Level impact/s to land, biodiversity, ecosystem services, water resources or air.	Minor medium- term social impacts on small number of people. Repairable damage or disturbance to property, structures or items. Minor infringement of culture heritage. Minor, temporarily human rights impact.
3	Moderate Level impact/s to land, biodiversity, ecosystem services, water resources or air.	Moderate medium- term social impacts or frequent social issues. Moderate damage to structures or items of local culture heritage significance/ scared locations. Moderate, temporary human rights impacts.
4	Significant Level impact/s (> 20 years) to land, biodiversity, ecosystem services, water resources or air.	A breakdown of social order. Widespread damage to items of global culture significance. Highly offensive infringements of culture heritage. Company directly responsible of complicit in severe, long term impacts on human rights

5	Permanent, severe impact/s to land, biodiversity, ecosystem services, water resources or air.	Complete breakdown of social order. Widespread desecration of items of global culture significance. Company directly responsible or complicit in severe and widespread long- term impacts on human rights

Table 5: Ratings for the assessment of likelihood

likelihood	Environment
Almost Certain	Could be incurred more than once in a year
Likely	Could be incurred over a 1-2 year timeframe
Possible	Could be incurred Within 5 year timeframe
Unlikely	Could be incurred in 5-20 year timeframe
Rare	Less than once in 20 year

The overall risk category was determined by making use of a matrix provided in table 6. Which taking into account the consequence and probability.

Table 6: Risk Assessment Matrix

Likelihood	Consequence				
	Level 1 Low level impact	Level 2 Minor impact	Level 3 Moderate impact	Level 4 Significant impact	Level 5 Severe impact
Almost certain	High (11)	High (16)	Extreme (20)	Extreme (23)	Extreme (25)
Likely	Moderate (7)	High (16)	High (17)	Extreme (21)	Extreme (24)
Possible	Low (4)	Moderate (8)	High (13)	Extreme (18)	Extreme (22)
Unlikely	Low (2	Low (5)	Moderate (9)	High (14)	Extreme (19)
Rare	Low (1)	Low (3)	Moderate (6)	High (10)	High (15)

Chapter Four
Results

Chapter Four

4 Results

4.1 Plant development and growth

Significant variation in number of leaves was observed (Table 7). Treatment X showed the highest average number of leaves (16.75 leaves per plant), while treatment 15X showed the lowest number of leaves per plant (12.83 leaves per plant) whereas no significant differences were observed for plant height.

Table 7: Number of leaves and plant height (cm) during 2014/2015 growing season.

Treatment	No. Leaves	Plant Height
Control	14.47^{b}	30.08^{a}
X	16.75^{a}	30.35^{a}
3X	13.57^{bc}	30.53^{a}
9X	13.41^{bc}	32.92^{a}
15X	12.83^{c}	32.82^{a}

Means in the same column with similar superscripets are not statistically different (Duncan test, $P \leq 0.05$).

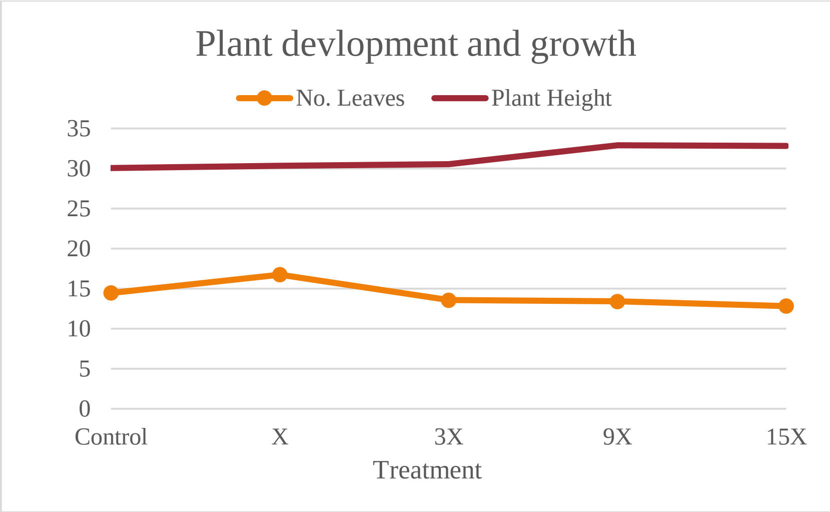


Figure 2: plant development and Growth for barely

4.2 Trace metals concentrations

4.2.1 In shoots (vegetative parts)

Table 8 showed the results of heavy (trace) elements in the plant vegetative parts. Cadmium (Cd) and Chromium (Cr) concentration was significantly increased in vegetative parts as their concentration increased in irrigation water. Treatment 15X showed the highest Cd and Cr concentration (1.27 and 18.55 ppm, respectively), whereas no significant differences were observed between control, X, 3X and 9X for Cd concentration (0.54, 0.74, 0.83 and 0.95 ppm, respectively) and no significant differences were observed between control, X and 3X for Cr concentration. Treatments X, 9X and 15X showed the highest Copper (Cu) concentration (48.40, 43.37 and 39.68 ppm, respectively) whereas the control and treatment 3X showed the lowest significant concentration (36.18 and 26.48 ppm, respectively).

Table 8: Heavy metals concentrations in shoots (ppm)

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn

Control	0.54^{b}	4.13^{c}	36.18b^{c}	1003.78^{a}	354070^{a}	469.96^{a}	5.31^{b}	3.66^{b}	129.07^{a}
X	0.74^{b}	5.31^{c}	48.40^{a}	943.04^{ab}	354070^{a}	442.00^{ab}	9.88^{ab}	4.50^{b}	124.25^{a}
3X	0.83^{ab}	6.59^{c}	26.48^{c}	750.33^{b}	354070^{a}	322.79^{b}	12.30^{a}	3.77^{b}	159.61^{a}
9X	0.95^{ab}	15.49^{b}	43.37^{ab}	751.79^{b}	354070^{a}	427.47^{ab}	6.29^{b}	4.85^{b}	139.55^{a}
15X	1.27^{a}	18.55^{a}	39.68^{ab}	960.45^{ab}	298348^{b}	323.90^{b}	6.30^{b}	7.94^{a}	106.26^{a}

Means in the same column with similar superscripts are not statistically different (Duncan test, $P \leq 0.05$).

Ferrous (Fe) concentration was significantly high in the control, 15X and X (1003.78, 960.45 and 943.04 ppm, respectively), in contrast treatments 3X and 9X had the lowest concentrations (751.79 and 750.33 ppm respectively). For Potassium (K), treatment 15X showed the lowest concentration (298348 ppm) whereas no differences were observed between the control, X, 3X and 9X treatments. The control, X and 9X showed the highest concentrations at Manganese (Mn) (469.96, 442.00 and 427.47 ppm, respectively) while, treatments 15X and 3X showed the lowest concentration (323.90 and 322.79 ppm, respectively). Nickel (Ni) concentration was significantly high in treatments 3X and X (12.30and 9.88 ppm respectively), whereas no significant differences were observed between the control and the other two treatments (9X and 15X). Treatment15X showed the highest significant concentration of Lead (Pb) (7.94 ppm), whereas no significant differences were observed between treatments 9X, X, 3X and control (4.85, 4.50, 3.77 and 3.66 ppm respectively).

In contrast to all trace metals added to the water, no significant differences were observed between treatments concentration at Zinc (Zn).

4.2.2 Roots

Table 9 showed the results of heavy (trace) elements in plant roots. Cadmium (Cd), Ferrous (Fe), Potassium (K) and Lead (Pb) concentration was significantly increased in plant roots as the concentration of these metals increased in irrigation water. No significant difference was observed between the control and treatments X and 3X in Cd, Cu and K.

Table 9: Heavy metals concentrations in root (ppm) of five treatments by ICP-M

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
Control	0.11^{b}	10.80^{cd}	10.28^{c}	2566.60^{b}	4530^{b}	156.30^{b}	13.33^{ab}	4.44^{bc}	45.87^{b}
X	0.03^{b}	5.88^{d}	7.83^{c}	1434.80^{c}	4852^{b}	59.68^{c}	6.56^{c}	1.94^{d}	20.50^{c}
3X	0.12^{b}	14.85^{c}	10.10^{c}	1569.30^{c}	6297^{ab}	92.90^{c}	8.09^{c}	3.34^{cd}	77.48^{a}
9X	0.73^{a}	68.94^{a}	19.60^{a}	3384.40^{a}	8022^{a}	211.22^{a}	15.13^{a}	5.73^{b}	50.89^{b}
15X	0.68^{a}	30.90^{b}	13.61^{b}	2898.70^{ab}	7138^{ab}	154.84^{b}	11.25^{b}	7.89^{a}	39.75^{b}

Means in the same column with similar superscripts are not statistically different (Duncan test, $P \leq 0.05$).

Treatment 9X showed the highest Cd, Cr, Cu, Fe, K, Mn and Ni concentration (0.73, 68.94, 19.60, 3384.40, 8022, 211.22 and 15.13 ppm, respectively). No significant differences were observed between control, X and 3X for Cu concentration (10.28, 7.83 and 10.10 ppm respectively). Treatments X and 3X showed no significant difference for Fe (1434.80 and 1569.30 ppm, respectively), Mn (59.68 and 92.90 ppm, respectively) and Ni (6.56 and 8.09 ppm, respectively) concentrations, which were the lowest. For K, treatments control and X were the lowest (4530 and 4852 ppm, respectively). Lead (Pb) concentration was significantly high in 15X (7.89), in contrast treatments X were the lowest (1.94 ppm). In contrast to all, treatment 3X showed the highest Zn concentration (77.48 ppm), and treatment X showed the lowest concentration (20.50 ppm).

4.2.3 Soil

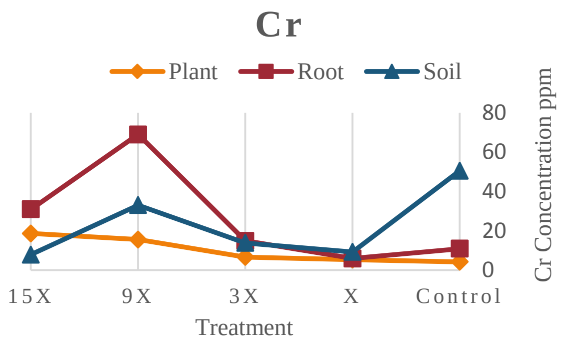
Table 10 showed the results of heavy (trace) elements in soil. The control treatment showed the largest concentration for all elements added to the irrigated water except for Cd and Zn. For Chromium (Cr), the highest concentration was (50.47 ppm) for the control treatment, whereas treatments X, 3X and 15X had lowest (9.21, 13.77 and 7.79 ppm, respectively). Copper (Cu) concentration was highest (19.19 ppm) for the control, in contrast treatments X, 3X and 15X had the lowest concentrations (5.73, 5.62 and 2.90 ppm, respectively). Ferrous (Fe) highest concentration was in the control (30812 ppm), whereas no significant differences were observed between X, 3X, 9X and 15X (6204, 7393, 15408 and 3051 ppm, respectively).

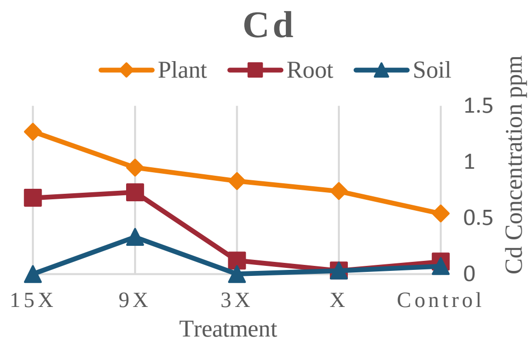
Table 10: Heavy metals concentrations in soil (ppm) of five treatments by ICP-M

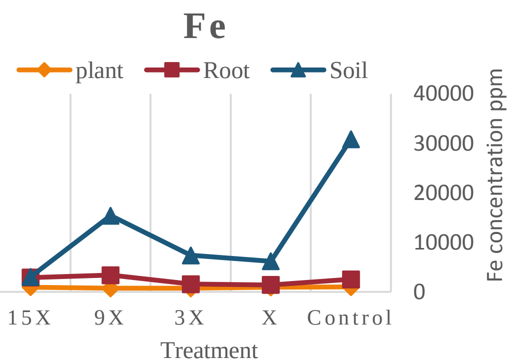
Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
Control	0.07^{b}	50.47^{a}	19.19^{a}	30812^{a}	6775^{a}	508.37^{a}	35.36^{a}	20.17^{a}	94.10^{a}
X	0.03^{b}	9.21^{c}	5.73^{c}	6204^{b}	2239^{b}	106.20^{bc}	8.29^{c}	5.22^{c}	35.90^{a}
3X	0.00^{b}	13.77^{c}	5.62^{c}	7393^{b}	1893^{b}	135.68^{bc}	9.04^{c}	4.97^{c}	35.90^{a}
9X	0.33^{a}	32.96^{b}	12.09^{b}	15408^{b}	6191^{a}	269.17^{b}	20.90^{b}	12.69^{b}	1607.80^{a}
15X	0.00^{b}	7.79^{c}	2.90^{c}	3051^{b}	1563^{b}	53.41^{c}	4.52^{c}	3.11^{c}	135.50^{a}

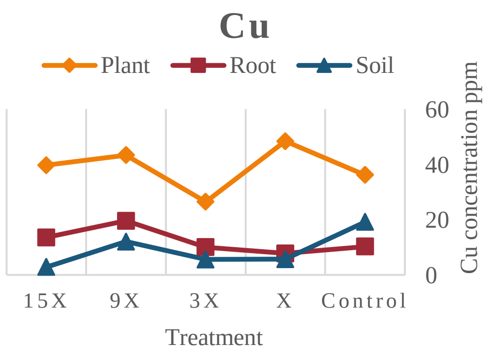
Means in the same column with similar superscripts are not statistically different (Duncan test, $P \leq 0.05$).

For Potassium (K), the control treatment and 9X showed the highest concentrations (6775 and 6191 ppm, respectively), whereas no significant differences were observed between X, 3X and 15X (2239, 1893 and 1563 ppm, respectively). Manganese (Mn) concentration was highest in the control (508.37 ppm), and lower for 15X (53.41 ppm). For Nickel (Ni) and Lead (Pb) concentrations, the control showed the highest concentrations (35.35 and 20.17 ppm, respectively) whereas treatment X, 3X and 15X showed the lowest concentrations (Ni: 8.29, 9.04 and 4.52 ppm, respectively, and Pb: 5.22, 4.97 and 3.11 ppm, respectively). Treatment 9X showed the highest Cadmium (0.33 ppm), whereas no significant differences were observed between control, X, 3X and 9X (0.07, 0.03, 0.00, 0.00 ppm, respectively). In contrast to all trace metals added to the water, no significant differences were observed between treatments concentration of Zinc (Zn).









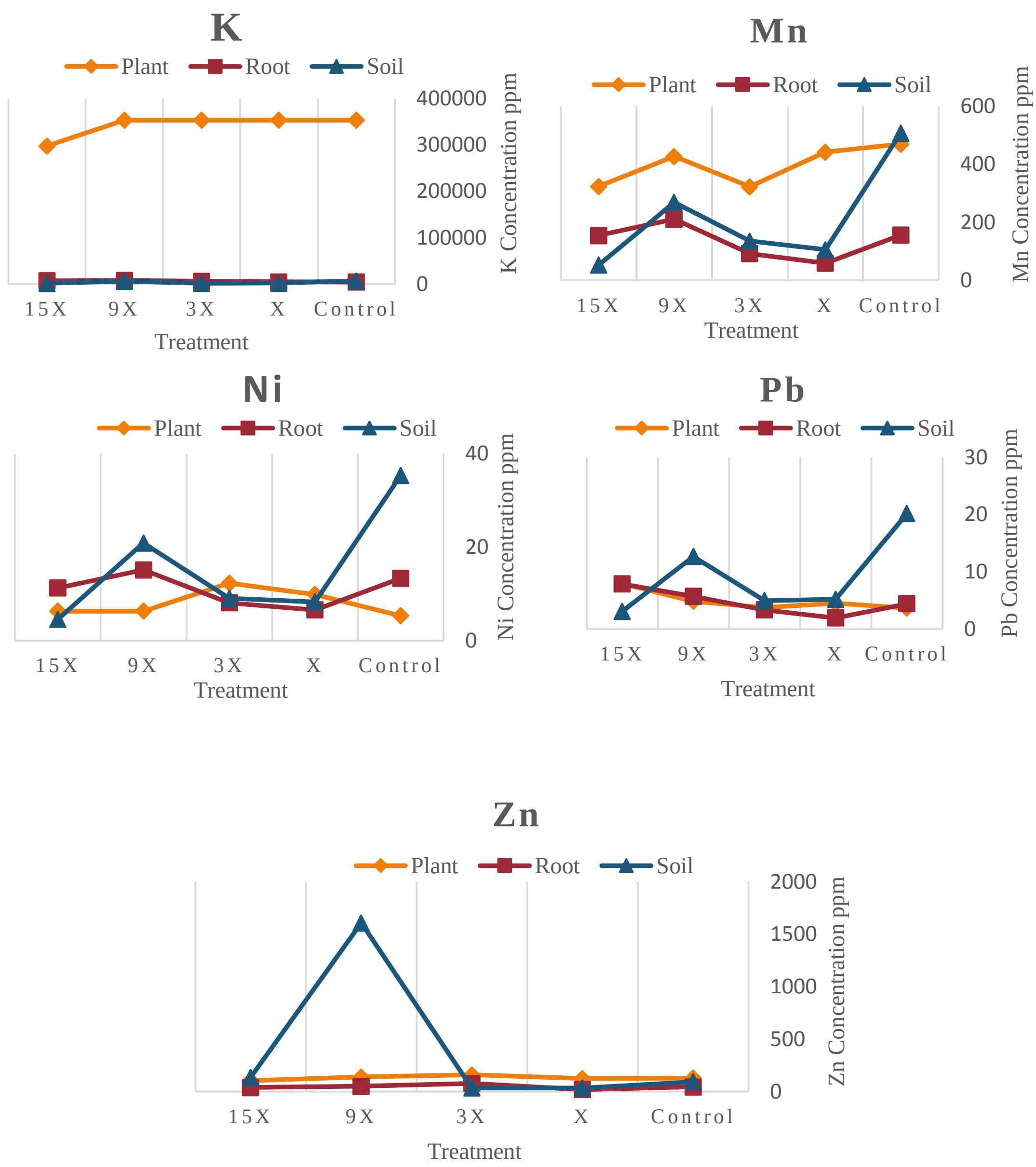


Figure 3: Concentration of heavy metals in plant, root and soil for barley

4.3 Model Development

The regression models for prediction of heavy metal concentrations in soil, shoots and roots from their concentrations in irrigation wastewater are in table 11.

Table 11: regression models for prediction of heavy metal concentrations in soil, shoots and roots

	Intercept	Slope	R- square	P- value
Soil				
cd	0.069	0.031	0.001	0.968
Cr	31.557	-64.738	0.146	0.525
Cu	12.876	-2.939	0.244	0.398
Fe	20821.407	-11685.930	0.251	0.390
K	5077.171	-11.187	0.107	0.591
Mn	344.373	-931.884	0.250	0.391
Ni	22.132	51.823	0.217	0.429
Pb	12.634	-26.924	0.429	0.471
Zn	178.578	368.333	0.339	0.577
Root				
cd	0.064	2.426	0.822	0.034
Cr	11.901	126.632	0.378	0.27
Cu	9.700	2.328	0.413	0.242
Fe	1874.324	874.498	0.425	0.233
K	5175.463	12.200	0.641	0.103
Mn	107.416	246.368	0.273	0.367
Ni	9.69	10.216	0.365	0.546
Pb	2.822	16.353	0.896	0.04
Zn	47.901	-1.075	0.033	0.958
Plant				
cd	0.632	2.076	0.923	0.009
Cr	4.145	51.654	0.965	0.003
Cu	37.893	0.828	0.016	0.839
Fe	839.181	-20.152	0.11	0.867
K	362214.207	255.178	0.704	0.076
Mn	-315.975	432.00	0.331	0.310
Ni	8.96	-8.428	0.358	0.554

Pb	3.497	12.775	0.912	0.03
Zn	140.098	-14.886	0.476	0.417

4.3.1 Cadmium Model

Table 11 gives us an important information in order to build our model. It provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 0.1, 82.2 and 92.3% for soil, root, and plant, respectively. The p-values were found to be for plant, root and soil (0.009, 0.034 and 0.968 respectively) $p > 0.005$ the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (cadmium concentration soil, root, plant)

X= the independent variable (cadmium concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

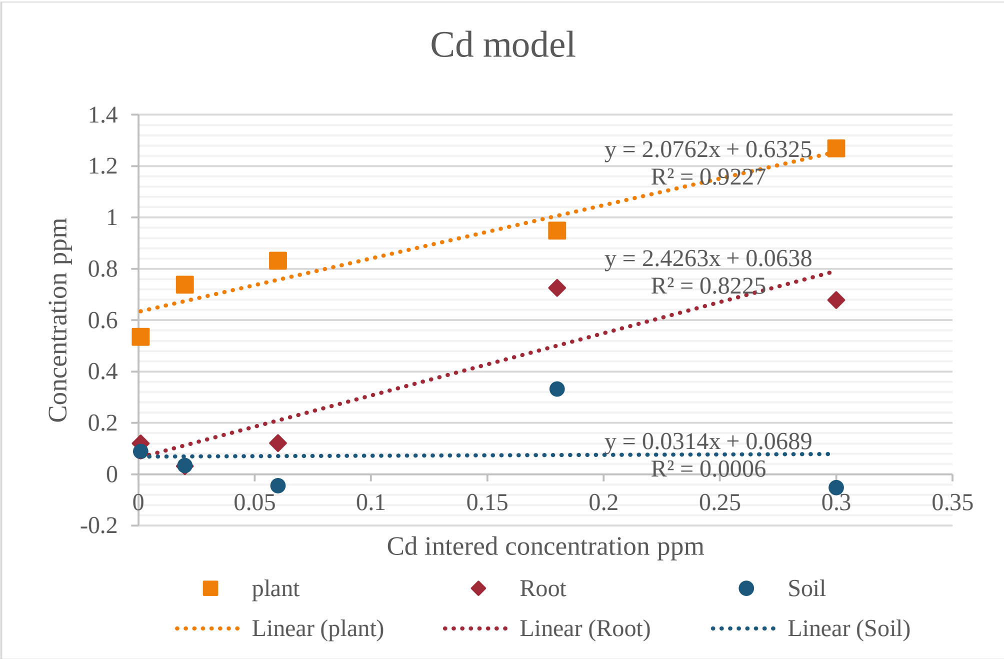


Figure 4: Cd model (regression analysis)

4.3.2 Chromium Model

Table 11 gives us an important information in order to build our model. It provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 14.60, 37.80, and 96.50 % for soil, root and plant, respectively. The p-values were found to be for plant equal to 0.003 which they are < .005, which means that there is a difference among plant means and p-value for soil and root (0.525 and 0.270 respectively) which are >.005 so, there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Chromium concentration soil, root, plant)

X= the independent variable (Chromium concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

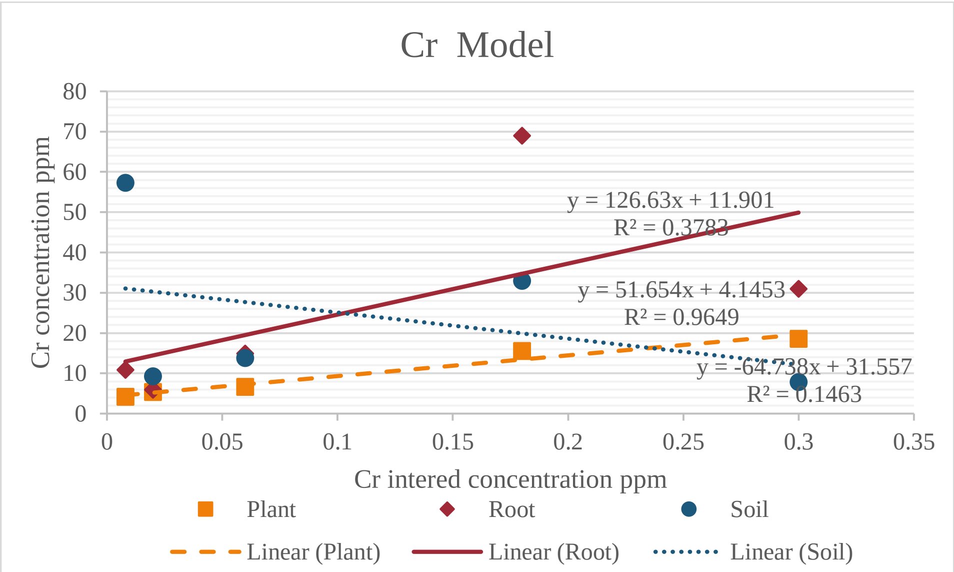


Figure 5: Cr model (regression analysis)

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4.3.3 Copper Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 24.40, 41.30, and 1.60 % for soil, root and plant, respectively. The p-values were found to be for plant, root and soil equal to 0.398, 0.242 and 0.839 respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Copper concentration soil, root, plant)

X= the independent variable (Copper concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

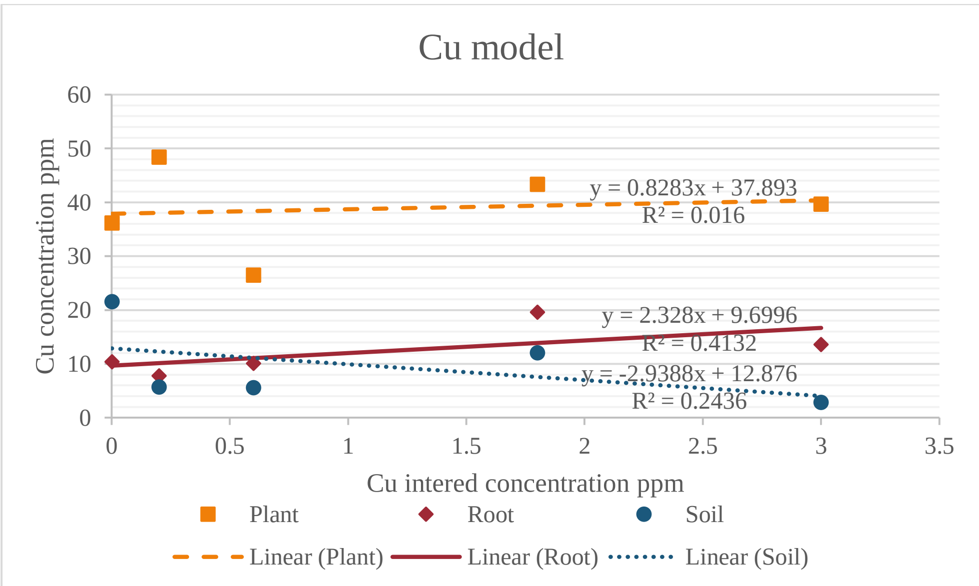


Figure 6: Cu model (regression analysis)

4.3.4 Iron Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 25.10, 42.50, and 11.00 % for soil, root and plant, respectively. The p-values were found to be for plant, root and soil equal to 0.390, 0.233 and 0.867 respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Iron concentration soil, root, plant)

X= the independent variable (Iron concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

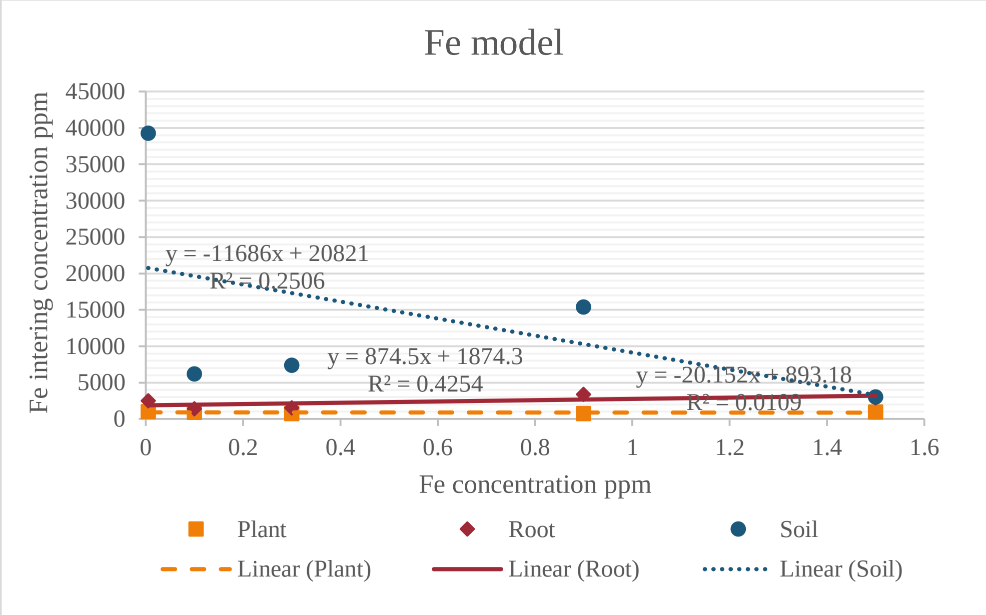


Figure 7: Fe model (regression analysis)

4.3.5 Potassium Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 10.70, 64.10, and 70.40 % for soil, root and plant, respectively. The p-values were found to be for soil, root and plant equal to 0.591, 0.103 and 0.076 respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Potassium concentration soil, root, plant)

X= the independent variable (Potassium concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

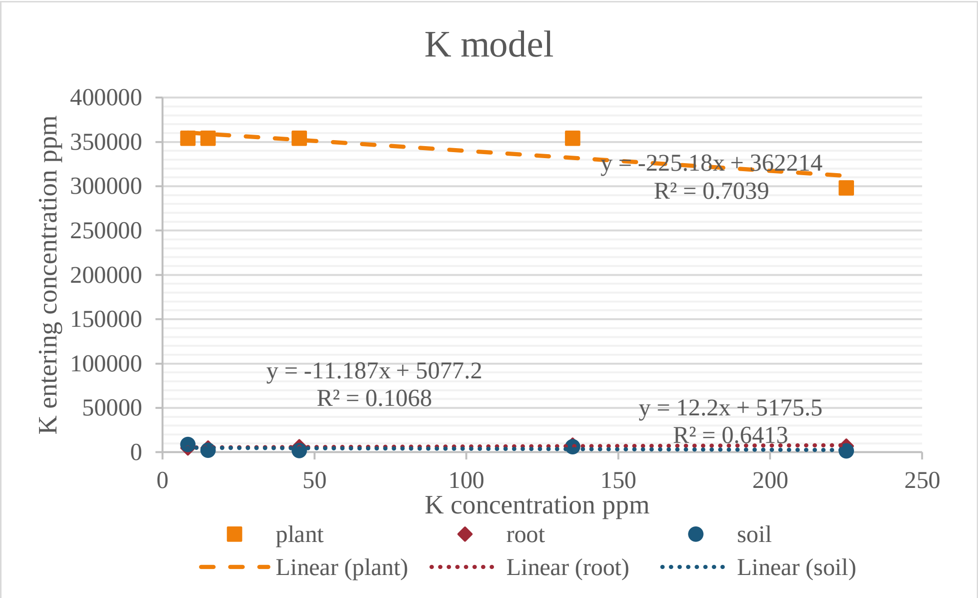


Figure 8: K model (regression analysis)

4.3.6 Manganese Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 25.00, 27.30, and 33.10 % for soil, root and plant, respectively. The p-values were found to be for soil, root and plant equal to 0.391, 0.367 and 0.310 respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Manganese concentration soil, root, plant)

X= the independent variable (Manganese concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

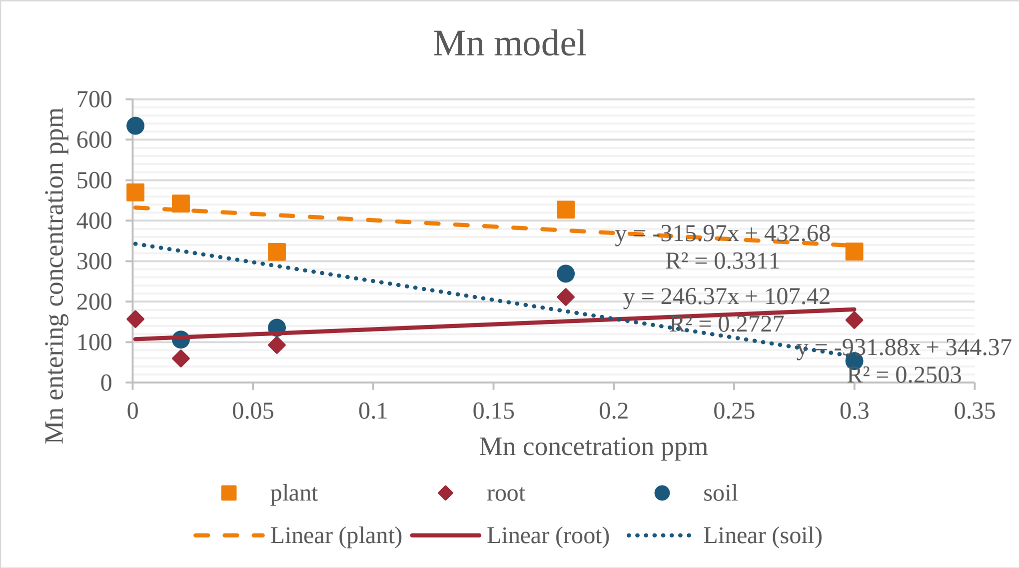


Figure 9: Mn model (regression analysis)

4.3.7 Nickel Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 21.70, 36.50, and 35.80 % for soil, root and plant, respectively. The p-values were found to be for soil, root and plant equal to 0.429, 0.546 and 0.554

respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Nickel concentration soil, root, plant)

X= the independent variable (Nickel concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

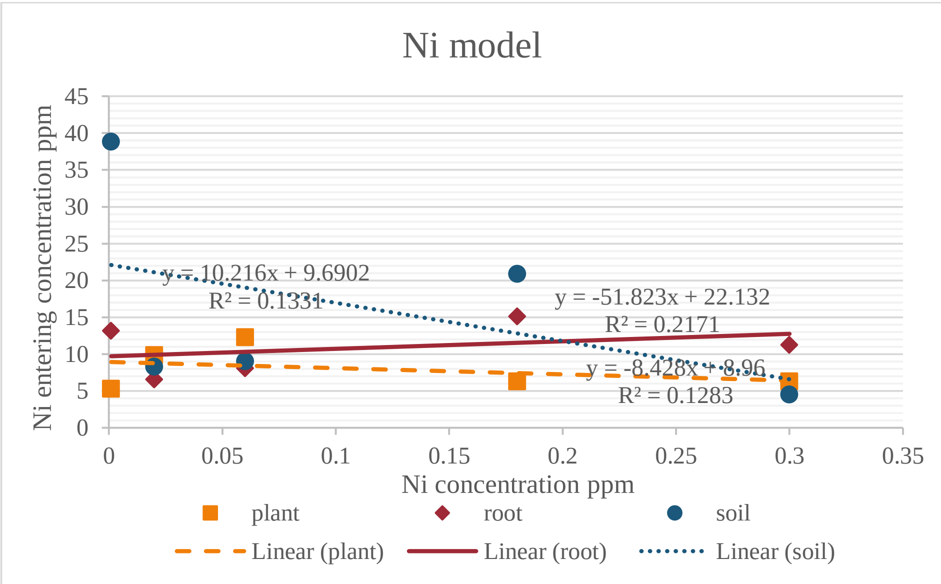


Figure 10: Ni model (regression analysis)

4.3.8 Lead Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were 42.90, 89.60, and 91.20 % for soil, root and plant, respectively. The p-values were found to be for soil, root and plant equal to 0.471, 0.04 and 0.030 respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Lead concentration soil, root, plant)

X= the independent variable (Lead concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

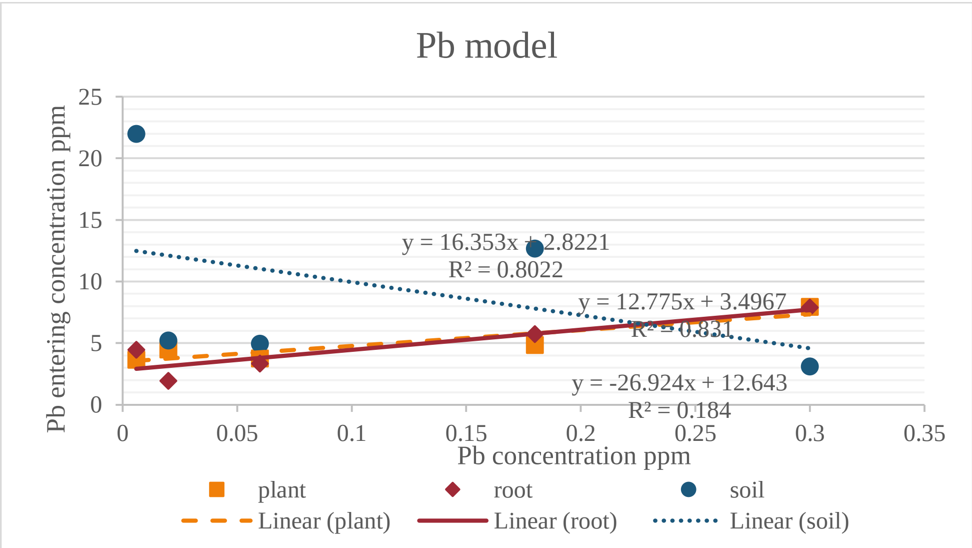


Figure 11: Pb model (regression analysis)

4.3.9 Zinc Model

Table 11 provides the intercept, slope, R^2 and P values for soil, root and plant. **R Square values** indicate how much of the total variation in the dependent variable is explained by the independent variable. These were

33.90, 3.30, and 47.60 % for soil, root and plant, respectively. The p-values were found to be for soil, root and plant equal to 0.577, 0.958 and 0.417 respectively, which they are >.005 the there is no significant difference among the means.

The general model is:

$$Y = a + bX$$

Where:

Y = the dependent variable (Lead concentration soil, root, plant)

X= the independent variable (Lead concentration in simulated water)

a = the intercept (Y value when X equal zero).

b = the slope (the regression coefficient).

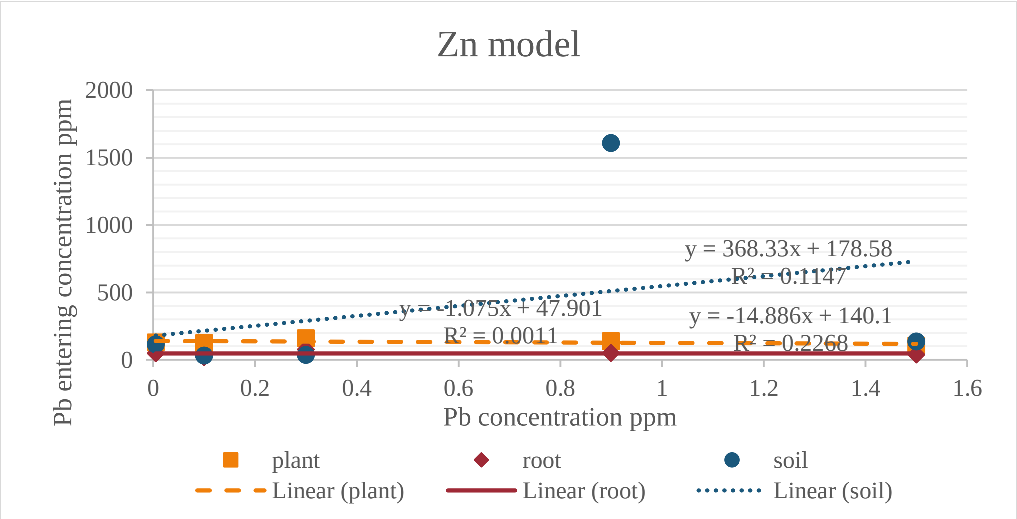


Figure 12: Zn model (regression analysis)

4.4 Factors

4.4.1 Enrichment Factor

The values of the enrichment factor (EF) in shoots are shown in Table 33 and in roots are shown in table (12).

The highest EF values in Barely shoots were: Cr: 2.35 at treatment 9X, Ni: 1.23 at treatment X, Pb: 1.64 at treatment 15X and Cu: 1.64 at treatment 9X.

In contrast, the lowest EF values in shoots were: Ni: 0.51 at treatment 9X, Cu: 0.55 at treatment 3X, Mn: 0.73 at treatment 3X and Zn: 0.76 at treatment 15X.

Table 12: Enrichment factors (EF)[a] of shoots of barley

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
X	1.38	1.28	1.34	0.94	1.00	0.94	1.86	1.23	0.96
3X	1.13	1.24	0.55	0.80	1.00	0.73	1.25	0.84	1.28
9X	1.14	2.35	1.64	1.00	1.00	1.32	0.51	1.29	0.87
15X	1.34	1.20	0.92	1.28	0.84	0.76	1.00	1.64	0.76

[a] Enrichment factor: ratio of metal concentration in plant of contaminated soil to shoots of uncontaminated soil.

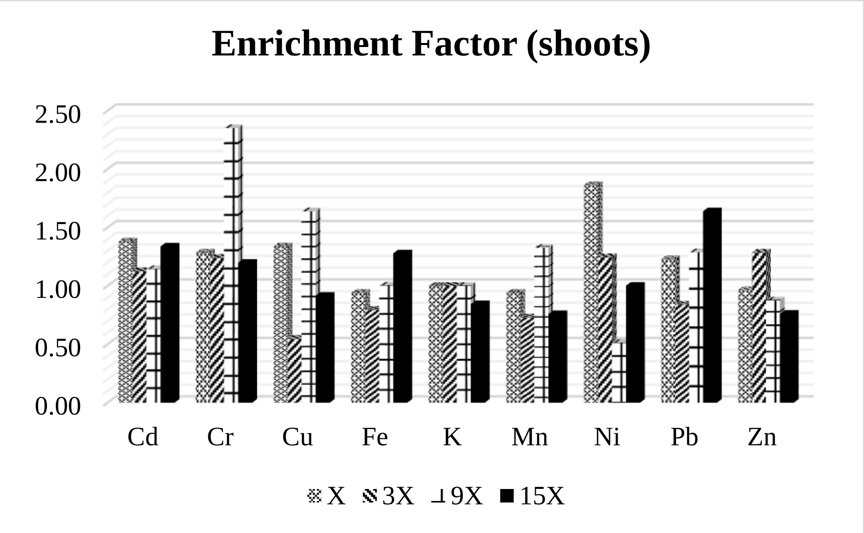


Figure 13: Enrichment Factor in shoots

Table 13: Enrichment Factor in barely roots

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
X	0.27	0.54	0.75	0.57	1.01	0.38	0.50	0.43	0.43
3X	3.77	2.52	1.29	1.09	1.30	1.56	1.23	1.73	3.78
9X	5.97	4.64	1.94	2.16	1.27	2.27	1.87	1.71	0.66
15X	0.93	0.45	0.69	0.86	0.89	0.73	0.74	1.38	0.78

The highest EF values in Barely roots (table 13) were: Cd: 5.97 at treatment 9X, Cr: 4.64 at treatment 9X, Zn: 3.78 at treatment 3X and Cd: 3.77 at treatment 3X.

In contrast, the lowest EF values in roots were: Cd: 0.27 at treatment X, Mn: 0.38 at treatment X, Pb and Zn: 0.43 at treatment X and Cr: 0.45 at treatment 15X.

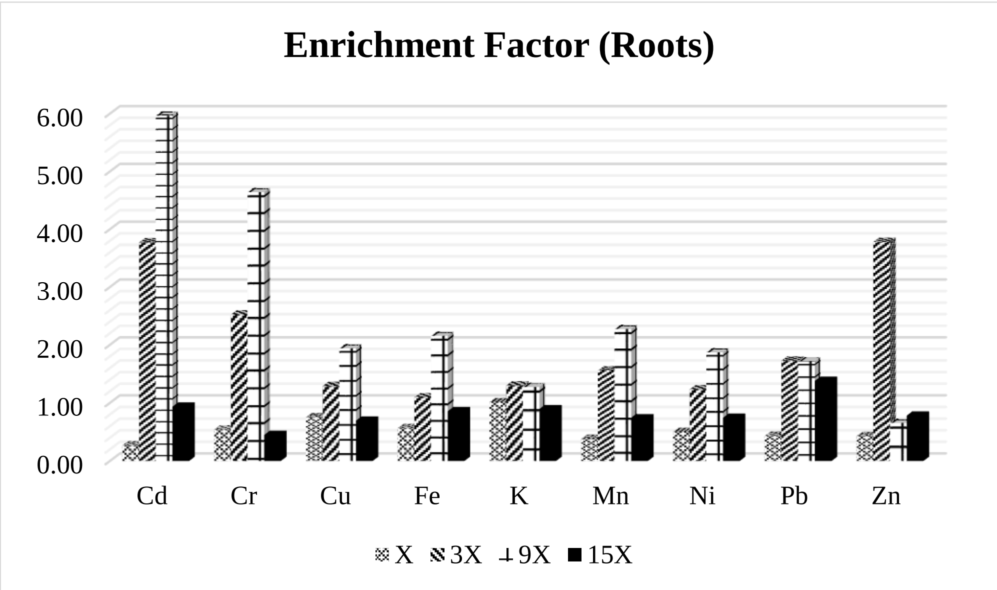


Figure 15: Enrichment Factor in roots

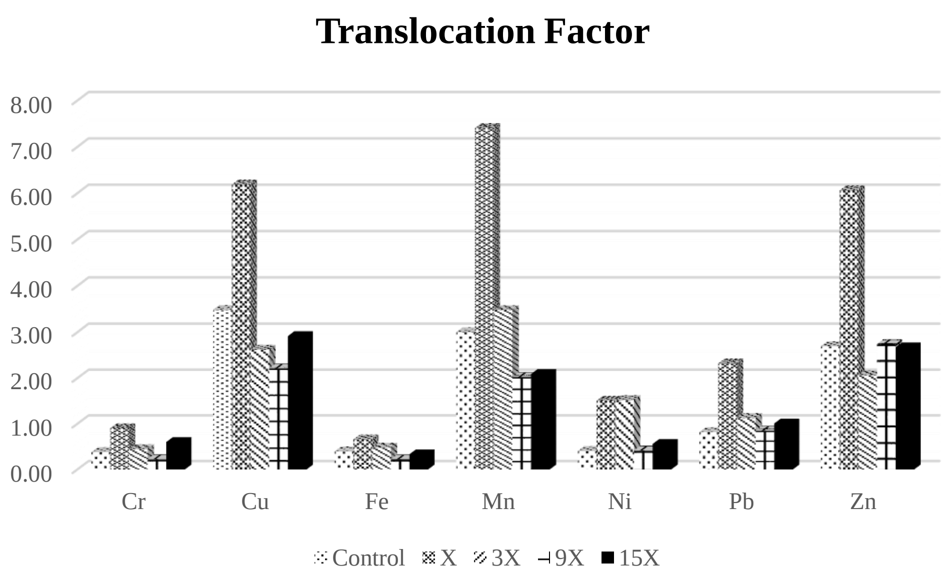
4.4.2 Translocation Factor

The metal translocation factor (TF) in barley is shown in Table 14. Among all values Potassium (K) had the highest TF for all treatments (73.87, 72.97, 56.23, 44.14 and 41.80). In contrast, the lowest TF values were Cr and Fe (0.22 at treatment 9X).

Table 14: Translocation Factor [a]

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
C	4.45	0.38	3.48	0.40	73.87	3.00	0.40	0.82	2.70
X	22.92	0.90	6.18	0.66	72.97	7.41	1.51	2.32	6.06
3X	6.84	0.44	2.62	0.48	56.23	3.47	1.52	1.13	2.06
9X	1.31	0.22	2.21	0.22	44.14	2.02	0.42	0.85	2.74
15X	1.87	0.60	2.92	0.33	41.80	2.09	0.56	1.01	2.67

[a] Translocation factor: ratio between the metal content in shoots and that in roots



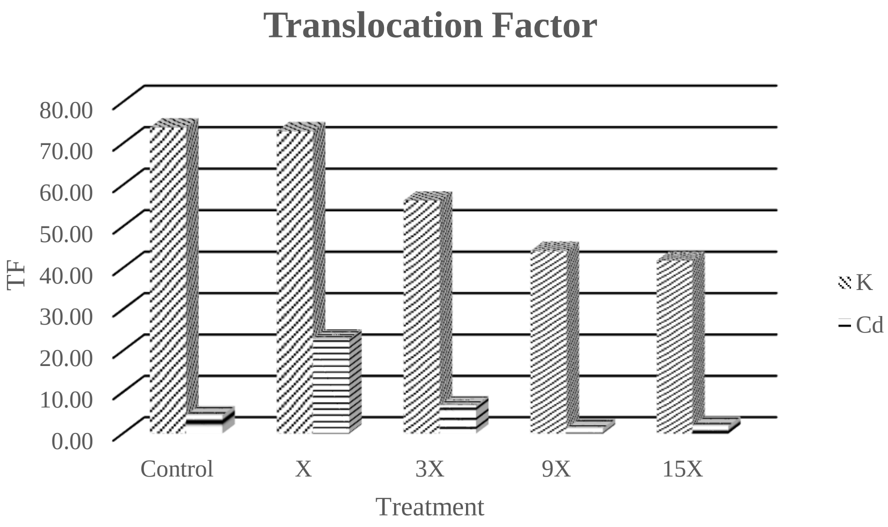


Figure 16: Translocation Factor

4.4.3 Bio concentration Factor

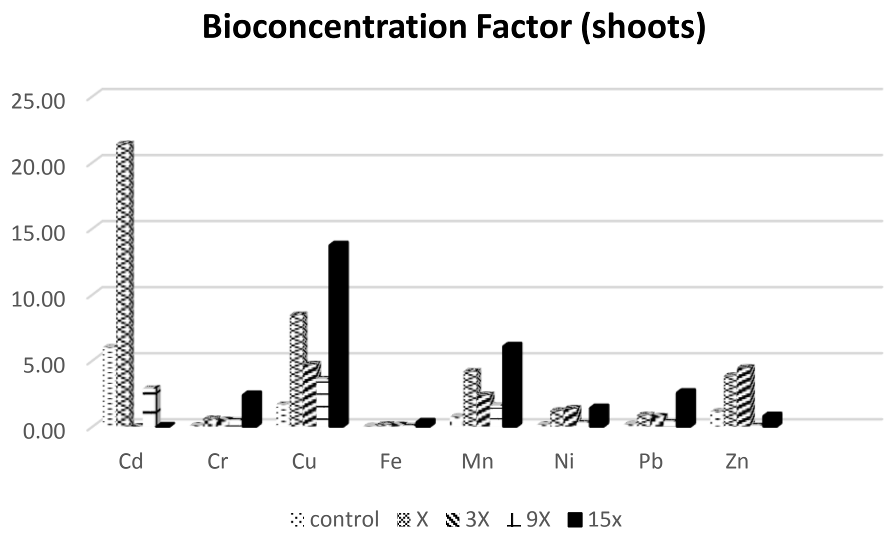
The values of Bio concentration Factor (BF) in shoots are shown in Table 36 and in roots are shown in Table 15.

The highest values of BF were: K: 190.90, 187.05 and 158.16 at treatments 15X, 3X and X respectively. On the other hand, the lowest BF were Fe: 0.03 and 0.05 for treatments control and 9X respectively.

Table 15: Bio concentration Factor in shoots [a]

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
control	5.99	0.07	1.68	0.03	40.65	0.74	0.14	0.17	1.13
X	21.38	0.58	8.45	0.15	158.16	4.16	1.19	0.86	3.84
3X	0.00	0.48	4.71	0.10	187.05	2.38	1.36	0.76	4.45
9X	2.87	0.47	3.59	0.05	57.20	1.59	0.30	0.38	0.09
15x	0.00	2.38	13.72	0.31	190.90	6.06	1.39	2.55	0.78

[a] Bio concentration factor: is defined as the ratio of the metal content in shoots and the total content in soil



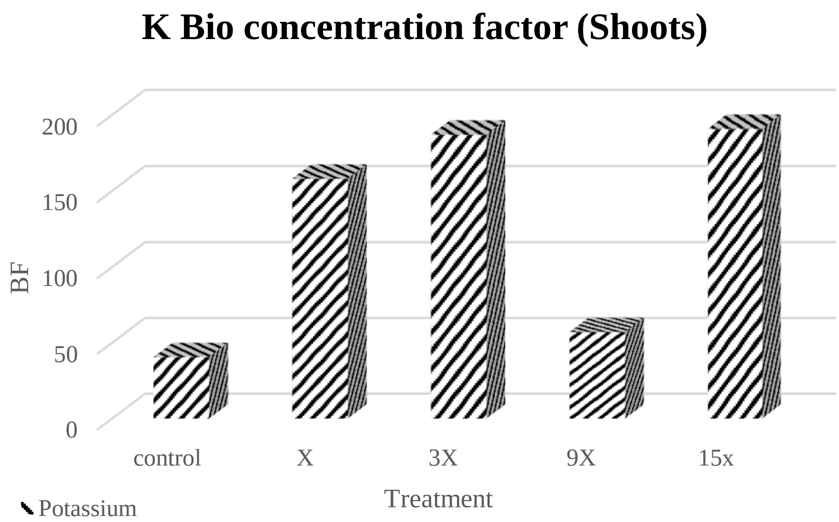


Figure 17: Bio concentration Factor in shoots

The highest values of BF in roots (table 16) were: Cu: 4.71, K: 4.57, Cr: 3.97, Mn: 2.90 and Pb: 2.54 and all for treatment 15X. On the other hand, the lowest BF were Cd: 0.00 at both 3X and 15X treatments, Fe: 0.06 for the control, Zn: 0.03 for 9X.

Table 16: Bio concentration Factor in Roots

Treatment	Cd	Cr	Cu	Fe	K	Mn	Ni	Pb	Zn
control	1.35	0.19	0.48	0.06	0.55	0.25	0.34	0.20	0.42
X	0.93	0.64	1.37	0.23	2.17	0.56	0.79	0.37	0.63
3X	0.00	1.08	1.80	0.21	3.33	0.68	0.89	0.67	2.16
9X	2.19	2.09	1.62	0.22	1.30	0.78	0.72	0.45	0.03
15x	0.00	3.97	4.71	0.95	4.57	2.90	2.49	2.54	0.29

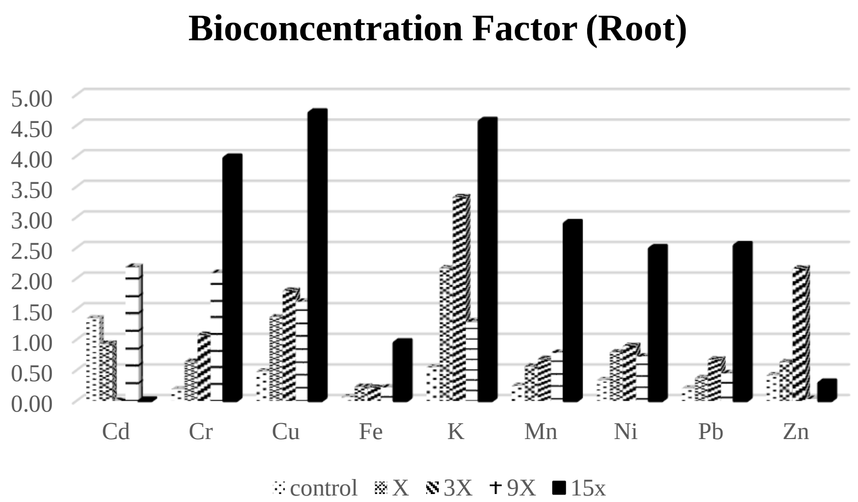


Figure 18: Bio concentration factor in roots

4.5 Environmental Risk Assessment

Using the AS/NZS ISO 31000: 2009 approach:

4.5.1 Environmental Risk Assessment

The consequence and likelihood of each risk is provided in accordance with rating system provided in table (4) and (5) respectively, and the overall risk rating is providing in accordance with matrix presented in table 17.

For the first risk (risk on soil) and according to the results which came from the experiment, there was no pollution on soil along the 15 years used.

For the second risk (risk on plant) and with based WHO regulations and the results from the experiment, there was a problem in Cd, Fe, Pb and Zn in all treatments.

Table 17: Environmental Risk Assessment

No.	Activity	Risk Description	Assumptions relevant to assessment of unmitigated risk	Consequence	likelihood	Risk
1	long time Irrigation with simulated treated wastewater containing heavy metals	Soil pollution and may leachate into ground water	WHO regulations	1	U	L (2)
		plant contamination and may cause health risk	WHO regulations	4	L	E (21)

4.5.2 Risk Treatment

In every project must has a number of measures in it is design in order to eliminate the project risks where possible, or reduce risks. In addition various mitigation measures should be applied.

Table 18: Risk Assessment with mitigation measures

No.	Activity	Risk Description	C1	L2	R3	Certainty in relation to effectiveness of mitigation
1	long time Irrigation with simulated treated wastewater containing heavy metals	Soil pollution and may leachate into ground water	1	U	L (2)	High certainty comparing the heavy metals concentration over the years with the thresholds made by WHO
		plant contamination and may cause health risk	2	P	M (8)	High certainty comparing the heavy metals concentration over the years with the thresholds made by WHO and use tertiary treatments to remove more heavy metals

C: Consequence, L: Likelihood, R: Risk

Chapter Five
Discussion

Chapter Five

5 Discussion

5.1 Evaluation of Water Quality

When using treated wastewater as a source of irrigation, factors such as contamination of plants and harvested product, the environment, public health need to be considered. For this purpose different guidelines were established by standard regulatory bodies such as World Health Organization (WHO), Food and Agricultural Organization (FAO) and others. These guidelines help to identify potential crop production problems associated with the use of conventional water sources in addition to soil and environmental ones. Applied water quality versus different standards is available in table (19).

Table 19: water levels of heavy metals used in the study compared to standards by different regulatory bodies (mg/L)

Element	PS	WHO	FAO	AUS. EPA	US EPA	Control	X	3X	9X	15X
K	-	0-78	0-2	0-78	0-78	8.30	15	45	135	225
Cd	0.01	0.01	0.01	0.01	0.01	0.001	0.02	0.06	0.18	0.3
Cr	0.10	0.55	0.10	1.00	0.10	0.0075	0.02	0.06	0.18	0.3
Cu	0.20	0.017	0.20	0.20	0.20	0.001	0.2	0.6	1.8	3.0
Pb	1.00	0.065	5.00	0.20	5.00	0.006	0.02	0.06	0.18	0.3
Mn	0.20	0.20	0.20	2.00	0.20	0.0011	0.02	0.06	0.18	0.3
Ni	0.20	1.40	0.20	0.20	0.20	0.001	0.02	0.06	0.18	0.3
Zn	2.00	0.20	2.00	2.00	2.00	0.0049	0.1	0.3	0.9	1.5
Fe	5.00	0.50	5.00	-	5.00	0.0049	0.1	0.3	0.9	1.5
PH	6- 9	6.5-8.5	6.50-8	6.50 -8	6	7.50	9.33	9.34	9.31	9.26

For the tap water (control) the heavy metals concentrations are lower than standards set by different agencies. Similarly, the pH is within the range of all standards.

According to EPA and WHO the maximum permissible K level of applied wastewater is between the range 0-78 mg/l, the applied water within the accepted limit until the third year effluent, then it became above the maximum.

Heavy metals level in the first year treatment plant effluent is higher than stated by different regulatory bodies guidelines for Cd. Also, Cu concentration is higher than the limit stated by WHO and meets the other regulatory guidelines (see table 19). Whereas, to concentrations of other elements are less than the limits.

For the third year simulated effluent, Cd and Cu concentrations are higher than the permissible limits for all agencies and this is similar for all effluent over the years. While, other elements concentrations are less than the maximum limit.

Concentration of Cr in the ninth and fifteenth year effluent is larger than the limits stated by PS, FAO and US EPA while it is lower than the other limits. Pb concentration exceeds the limits stated by WHO in the ninth year effluent, also it exceeds the limits stated by WHO and AUS EPA in the fifteenth year. Mn and Ni concentration exceeds the limit in the fifteenth year effluent at all limits except for AUS EPA and WHO respectively. Zn and Fe concentrations remain lower than the maximum level except for WHO standards in the ninth and fifteenth years effluent.

PH of all wastewater treatment plant effluent over the years was larger than the normal range stated by the different agencies. Results also indicated that pH values decreased with time, this decrease may be attributed to the increase of organic loads and decline of its removal efficiency as the treatment plant are heavily overloaded year after another .It may also results from the formation of volatile acids and carbon dioxide from anaerobic digestion of organic matter (Abu Nada, 2009).

5.2 Plant development and growth

Compared to crop grown, in the control the number of leaves was significantly higher. The highest number of leaves was produced in treatment X, however, longer period of wastewater application (3- 15 years) resulted in significant lower number of leaves production than the control. Researchers showed that with the Cd pollution in spring barley increased whereas plants quantity decreased to 80% of the initial quantity, and some investigations showed that nonessential doses of Pb did not inhibit biomass production but stimulated plant growth as well as micronutrients (Ryzhenko et al., 2015).

Rusan et al., (2007) reported that the biomass production was significantly higher in the control and the highest biomass was produced after 5 years of annual treating and longer treating period produced lower biomass but still larger than the control.

On the other hand, the metals used did not affect plant height of barley. These results are in agreement with the results obtained by González and Lobo, (2013) who found that the differences observed in barely height between the anthesis and grain filling stages were very small and were not significant in the four genotypes studied, whereas Mahmood et al, (2007) reported that adding Cu, Zn and Pb to barley affected the height of the plant and the highest high was obtained after 5 years of wastewater application.

5.3 Concentrations of trace metals in shoots (vegetative part)

The results from this study indicated that heavy metal level in the applied water varies with time Table 3. The results also indicated that Cd, Cr and Pb uptake increased significantly in comparison with the control contents. The highest metal content was in the plant grown in the soil receiving treated wastewater for 15 years. Research showed an increase in trace metals uptake by the shoots irrigated with sewage water than that irrigated with ground water (Rusan et al., 2007).

Rusan et al., (2007) reported that the concentrations of Cd and Pb were higher with wastewater application, also González and Lobo, (2013) reported the same results for Cd and Cr in barley.

Data showed that in all treatments, Cadmium and Lead concentrations are more than the permitted level by WHO (Table 20), so the plant are not suitable for consumption, these results are in agreement with those obtained by Rusan et al., (2007), also González and Lobo, (2013) reported the same result for Cd. However, Brunetti et al., (2012) showed concentrations lower than WHO Levels in barely. Plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield (Bigdeli and Seilsepour, 2008).

Chromium concentrations in all treatments were below their respective WHO maximum permissible levels and this is in agreement with the results obtained by Brunetti et al., (2012).

Micronutrient contents (Cu, Zn, Fe, and Mn) of the plants are essential for plant nutrition although they are required by the plants in relatively much smaller amounts compared to macronutrients (Rusan et al., 2007). Inconsistent results were found for these micronutrients. Cu content in the plant were the highest in the effluent of the treatment plant. Studies showed that plants grown in Cu-contaminated soil usually accumulate an elevated Cu content in their tissue (Xiong and Wang, 2005).

Mn and Fe had the highest level when irrigating by the tap water then they started to decline over the years. This can be explained by the “concentration/dilution effect” induced with relatively lower biomass (Rusan et al., 2007).

Researches indicated that for Cu, Zn, Fe, Mn contents in the barley plant were the highest in the plant grown in the soil receiving wastewater after 2 years. However the concentrations of these metals significantly reduced in the plants grown in the soil received wastewater for longer period namely for 5–10 years (Rusan et al., 2007).

Data showed that there was pollution relative to WHO standard levels in all treatments for Zn and Fe minerals. Previous researches found no pollution for Zn (Rusan et al., 2007) and (Brunetti et al., 2012). Whereas, González and Lobo, (2013) reported that there was a pollution for Zn in barely varieties. For Fe Rusan et al., (2007) reported similar results as this research.

Also, (Chiroma et al., 2014) reported that the concentrations of Fe and Zn in different parts of okro are above the maximum permissible level set by WHO. Long et al., (2003) reported for three selected crops (cabbage, celery and Spinach) showed that excess Zn in growth media caused toxicity to all three crops (Long et al., 2003).

The Mn and Cu concentrations in all treatments are below the WHO maximum permissible levels. And this is in agreement with the previous researches (Rusan et al., 2007, Brunetti et al., 2012).

Also, Bao et al., (2014) reported similar results for Cu in Winter Wheat plant. Ni concentrations in all treatments were below the maximum permissible limit recommended by WHO which shows no negative effects and this is in agreement with results in previous research (Brunetti et al., 2012). K maintained the same concentration over the time until reaching the fifteenth year irrigation, it declined.

5.4 Trace metals concentrations in roots

In general, the concentration of heavy metals in roots increased consistently with the metal total contents in the soil.

Root results indicated that for Cd, Cr, Cu, Fe, K, Mn and Ni the highest content was after 9 years from the irrigation by treated gray water. However the concentrations of these metals significantly reduced in the roots of barely grown in the soil received wastewater for longer period, namely for 15years. For Pb metal, concentration was the highest after irrigation for 15 years and for Zn content in the root there contrary to soil and plant, where the highest content was after irrigating for 3 years and then the concentration started to decline for longer period namely for 9- 15 years.

Cadmium, Copper, Potassium, Manganese and zinc accumulation in all treatments in the aerial vegetative parts of the plant was higher than in the roots. This is in agreement with literature data the same result for different vegetables for Cd and Mn (Bigdeli and Seilsepour, 2008), a significantly higher concentration of cadmium in barley roots than in straw was observed by Sêkara et al., (2005). According to Brunetti et al., (2012) the contents in roots were always higher than those in shoots. Also, González and Lobo, (2013) found that different varieties of barely had higher concentration in roots than in stem.

Cu levels in both root and shoot increased, but shoot Cu concentration increased more sharply than root with increasing Cu levels in growth media (Xiong and Wang, 2005) found that Cu concentration in the shoots was significantly influenced by Cu concentration in soil and increased markedly with an increase in the soil Cu concentration. Also they showed that plants grown in Cu-contaminated soil usually accumulate an elevated Cu content in their tissue (Xiong and Wang, 2005). Zn concentration in four variety of barely was observed by (González and Lobo, 2013) which they founded that in all treatments the zinc concentrations were larger in the root.

The concentration of Chromium and iron was always higher in roots than in the vegetative parts. (Shanker et al., 2005) Reported the same result for Cr. This could be because Cr is immobilize in the vacuoles of the root cells, thus rendering is less toxic, which may be a natural toxicity response of the plant

(Shanker et al., 2005). The same observation was reported by other researchers (Brunetti et al., 2012) who investigated metal accumulation in barely irrigated with waste water and got the higher accumulation of Cu and Zn in root of compared to other plant parts. The same results were obtained by González and Lobo, (2013). For Fe metal (Chiroma et al., 2014) observed same observation when investigating the metal accumulation in Bush green and Roselle plants. Maximum Nickel concentration in roots was observed in the control and after irrigation for nine and fifteen years respectively. Also the maximum Lead concentration was observed in the control and after irrigation for nine years. These results are in agreement with results reported by (Chiroma et al., 2014) for Lead concentration in Bush green and Roselle. (Brunetti et al., 2012) and that the contents in roots were always higher for barley plant than those in shoots. Also (Sêkara et al., 2005) found that Lead concentration in the root of barely is larger than in the shoots.

The mean concentrations of Fe and Pb in plant roots in all treatments were above the maximum levels of the recommendations of WHO. These results are in agreement with the findings of Chiroma et al. (2014) for Bushgreen and Roselle plants and Brunetti et al. (2012) for barley and wheat.

Cd concentration in all treatments (except the irrigation using the effluent of WWTP) were above the maximum levels of recommendations of WHO. This is in agreement with what was detected by González and Lobo (2013) and Nazir et al. (2015).

On the other hand, the concentrations of Cu, Mn, Ni and Zn in all treatments were below the maximum permissible level. The same results were reported by Brunetti et al. (2012) for Ni, Cu and Zn, Nazir et al. (2015) reported the same result for Cu when Tamarixaphyda, Dodonaea viscose, Acacia modesta, Xanthium strumarium were studied.

Cr concentration in all treatments (except the irrigation for nine years) were also below the maximum permissible limits indicated by WHO. This is in agreement with what was detected by González and Lobo, (2013) in Pedrezuela variety and Brunetti et al. (2012) in barley and Nazir et al. (2015).

5.5 Trace metals concentrations in soil

The highest concentration was found in soils irrigated with tap water except for Cd and Zn. This indicated that originally the soil contains elevated amounts of these elements and irrigation leached these elements down the soil profile. Previous studies reported that the movement of heavy metals in soils irrigated with wastewater is very slow (Ebrahim et al., 2016). Similar results was reported by Ebrahim et al. (2016) and Dikinya and Areola (2010). Whereas, González and Lobo (2013) showed that the amount of metal that remained in the soil was greatest for the higher concentration of Zn and Cd treatments.

No significant differences were found in the concentration of Zn between the treatments. This is in agreement with the results reported by Ebrahim et al., (2016), Rusan et al., (2007) and Mohammad and Mazahreh, (2003).

All heavy metals had concentrations in soil marginally below the maximum permissible level (see table 44). This is in agreement with results reported by Bigdeli and Seilsepour, (2008), (Ebrahim et al., 2016) and (Chiroma et al., 2012). The obvious implication of this observation is that there is no threat of soil contaminations by these metals when the effluent of the treatment plant is used for the irrigation of barely.

The highest Cd, Cu and K concentration for these metals was in vegetative parts and the lowest in soil over the years. Whereas, Fe concentration was the highest in soil and lowest in shoots.

Table 20: maximum permissible limits in soil, plant and root by WHO

Heavy metal	Soil Guidelines (mg/kg)	Plant and Root Guidelines (mg/kg)
Cd	3	0.1
Cr	100	50
Cu	100	73
Fe	50000	425
Mn	2000	500
Ni	50	67
Pb	100	0.3
Zn	300	100

5.6 Factors

5.6.1 Enrichment Factor

Enrichment factor (EF) has been calculated to derive the degree of soil contamination and heavy metal accumulation in soil and in plants growing on contaminated sites compared to soil and plants growing on uncontaminated soil (Singh et al., 2010).

The EF values in shoots (Table 12) indicated that for Cd and Cr higher metal enrichment capability in shoots grown in contaminated soil in all treatments and this is in agreement with the results indicated by Brunetti et al., (2012).

For Cu, higher enrichment capability in contaminated soil was founded when irrigated with the effluent of waste water treatment plant for nine years. In contrast, the other treatments gave a higher enrichment capability in uncontaminated soils.

For Fe, a higher enrichment capability was found when irrigating with simulated effluent water from waste water treatment plant for fifteen years in contaminated soil. And the nine years simulated effluent has an equal concentrations in both contaminated and uncontaminated soil. The rest of treatments gave a higher enrichment capability in uncontaminated soils.

For Mn, all treatments except the nine years simulated effluent a higher enrichment capability was found in uncontaminated soil.

For Ni, a higher enrichment capability was found when irrigating with nine years simulated effluent water from waste water treatment plant in uncontaminated soil. And the fifteen years simulated effluent has an equal concentrations in both contaminated and uncontaminated soil. The rest of treatments gave a higher enrichment capability in contaminated soils.

For Pb, in all treatments except the three years simulated effluent a higher enrichment capability was found in contaminated soil. For Zn, in all treatments except the three years simulated effluent a higher enrichment capability was found in uncontaminated soil.

The EF roots values (Table 13) indicated that when irrigating with treatment effluent water the roots have higher enrichment capability in uncontaminated soil except for K.

Also, when irrigating with fifteen years simulated waste water treatment plant effluent roots have higher enrichment capability in uncontaminated soil except for Pb.

On the other hand, and when irrigating with three and nine years simulated effluent roots have higher enrichment capability in contaminated soil except for Zn at nine years.

5.6.2 Translocation Factor

This factor was calculated to determine relative translocation of metals from soil to plant parts (root and shoot) (Singh et al., 2010).

Also it illustrates the efficiency of the internal transport of metals from roots to shoots. A value > 1 indicates that the plant is a metal accumulator appropriate for phytoextraction (Brunetti et al., 2012).

In general all metals had a translocation factor >1 in all treatments except Cr and Fe which had TF values < 1 in all treatments and Ni and pb when irrigating with tap water and nine and fifteen years simulated treated wastewater. Previous researchers reported that Cd, Cr, Cu, Ni, Pb and Zn have values < 1 (Brunetti et al., 2012).

Chapter Six

Chapter Six

6 Conclusion

The main objective of this study was to investigate the impacts of long term use of treated wastewater irrigation on soil and Barley parts. Based on the results obtained from field measurements and historical data the following can be concluded.

1- Soil and crop quality parameters are significantly affected by long-term wastewater irrigation.

2- Heavy metal accumulation differed according to the part of the plant.

3- Continuous irrigation with treated wastewater may lead to accumulation of heavy metals beyond crop tolerance levels in plant organs Therefore, these concerns should be essential components of any management of wastewater irrigation, and heavy metals concentrations in soil were below WHO standards.

4- Cd, Fe and Pb concentrations in plant organs (shoots and roots) were noticeably larger than the WHO standards.

5- Most translocation factor values where higher than 1, indicating that the barley is suitable for phytoremediation.

6- Whereas, Cr, Fe, Ni and Pb need further investigation on suitability of barley for phytoremediation.

7- Proper management of wastewater irrigation and periodic monitoring of soil fertility and quality parameters are required to ensure successful, safe long term reuse of wastewater for irrigation.

8- Environmental risk in soil was found low. This may be different on the long term.

9- Environmental risk in organs existed in variable levels and mitigation was recommended.

10- The treated wastewater can be used to irrigate the cultivars that do not consumed by humans or animals such as: grass

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Annexes

A1: Palestinian Standards for Treated Wastewater

الخاصية ملجم/لتر ما لم يذكر غير ذلك	تصريف إلى البحار على بعد 500 متر	تغذية الخزان الجوفي بالترشيح	ري أعلاف جافة	ري أعلاف خضراء	ري حدائق ملاعب و متنزهات	ري محاصيل صناعية و حبوب	ري أشجار حرجية و غابات	ري أشجار حمضيات	ري أشجار زيتون	ري أشجار لوزيات
الألمنيوم Al	**5**	**1**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
الزرنيخ Ar	**0.05**	**0.05**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
النحاس Cu	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**
الحديد Fe	**2**	**2**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
المنغنيز Mn	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**
النيكل Ni	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**
الرصاص Pb	**0.1**	**0.1**	**1**	**1**	**0.1**	**1**	**1**	**1**	**1**	**1**
السيلينيوم Se	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**
الكادميوم Cd	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**
الزنك Zn	**5**	**5**	**2**	**2**	**2**	**2**	**2**	**2**	**2**	**2**
السيانيد CN	**0.1**	**0.1**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**
الكروم Cr	**0.5**	**0.05**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
الزئبق Hg	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**
كوبالت Co	**1**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**
البورون B	**2**	**1**	**0.7**	**0.7**	**0.7**	**0.7**	**0.7**	**0.7**	**0.7**	**0.7**

A2: Threshold levels of trace elements for crop production (FAO)

(Pescod, 1992) --- *FAO*

Element		**Recommended maximum concentration (mg/l)**	**Remarks**
Al	(aluminium)	5.0	Can cause non-productivity in acid soils (pH < 5.5), but more alkaline soils at pH > 7.0 will precipitate the ion and eliminate any toxicity.
As	(arsenic)	0.10	Toxicity to plants varies widely, ranging from 12 mg/l for Sudan grass to less than 0.05 mg/l for rice.
Be	(beryllium)	0.10	Toxicity to plants varies widely, ranging from 5 mg/l for kale to 0.5 mg/l for bush beans.
Cd	(cadmium)	0.01	Toxic to beans, beets and turnips at concentrations as low as 0.1 mg/l in nutrient solutions. Conservative limits recommended due to its potential for accumulation in plants and soils to concentrations that may be harmful to humans.
Co	(cobalt)	0.05	Toxic to tomato plants at 0.1 mg/l in nutrient solution. Tends to be inactivated by neutral and alkaline soils.
Cr	(chromium)	0.10	Not generally recognized as an essential growth element. Conservative limits recommended due to lack of knowledge on its toxicity to plants.
Cu	(copper)	0.20	Toxic to a number of plants at 0.1 to 1.0 mg/l in nutrient solutions.

F	(fluoride)	1.0	Inactivated by neutral and alkaline soils.
Fe	(iron)	5.0	Not toxic to plants in aerated soils, but can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum. Overhead sprinkling may result in unsightly deposits on plants, equipment and buildings.
Li	(lithium)	2.5	Tolerated by most crops up to 5 mg/l; mobile in soil. Toxic to citrus at low concentrations (<0.075 mg/l). Acts similarly to boron.
Mn	(manganese)	0.20	Toxic to a number of crops at a few-tenths to a few mg/l, but usually only in acid soils.
Mo	(molybdenum)	0.01	Not toxic to plants at normal concentrations in soil and water. Can be toxic to livestock if forage is grown in soils with high concentrations of available molybdenum.
Ni	(nickel)	0.20	Toxic to a number of plants at 0.5 mg/l to 1.0 mg/l; reduced toxicity at neutral or alkaline pH.
Pd	(lead)	5.0	Can inhibit plant cell growth at very high concentrations.
Se	(selenium)	0.02	Toxic to plants at concentrations as low as 0.025 mg/l and toxic to livestock if forage is grown in soils with relatively high levels of added selenium. As essential element to animals but in very low concentrations.
Sn	(tin)		
Ti	(titanium)	-	Effectively excluded by plants; specific tolerance unknown.
W	(tungsten)		
C	(vanadium)	0.10	Toxic to many plants at relatively low concentrations.
Zn	(zinc)	2.0	Toxic to many plants at widely varying concentrations; reduced toxicity at pH > 6.0 and in fine textured or organic soils.

A3: Guidelines for irrigation water Quality (FAO).

GUIDELINES FOR IRRIGATION WATER QUALITY (FAO, 1992)

Water parameter	Symbol	Unit[1]	
SALINITY			
Salt Content			
Electrical Conductivity	EC_w	dS/m	0 – 3
(or)			
Total Dissolved Solids	TDS	mg/l	0 – 2000
Cations and Anions			
Calcium	Ca^{++}	me/l	0 – 20
Magnesium	Mg^{++}	me/l	0 – 5
Sodium	Na^{+}	me/l	0 – 40
Carbonate	CO^{--}_3	me/l	0 – .1
Bicarbonate	HCO_3^{-}	me/l	0 – 10
Chloride	Cl^{-}	me/l	0 – 30
Sulphate	SO_4^{--}	me/l	0 – 20
NUTRIENTS2			
Nitrate-Nitrogen	NO_3-N	mg/l	0 – 10
Ammonium-Nitrogen	NH_4-N	mg/l	0 – 5
Phosphate-Phosphorus	PO_4-P	mg/l	0 – 2
Potassium	K^{+}	mg/l	0 – 2
MISCELLANEOUS			
Boron	B	mg/l	0 – 2
Acid/Basicity	pH	1–14	6.0 – 8.5
Sodium Adsorption Ratio[3]	SAR	(me/l)[1], [2]	0 – 15

جامعة النجاح الوطنية
كلية الدراسات العليا

تقييم المخاطرة ونمذجة امتصاص العناصر الثقيلة من قبل نبات الشعير المروي بمياه تحتوي على عناصر ثقيلة

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قدمت هذه الاطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في هندسة المياه والبيئة بكلية الدراسات العليا في جامعة النجاح الوطنية , نابلس فلسطين
2017

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الملخص

تم تطبيق هذه التجربة من اجل دراسة تأثير الري طويل الامد باستخدام المياه التي تخرج من محطة التنقية بعد معالجتها على التربة والنبات والجذور على نبات الشـــعير, من اجل تقييم ونمذجة الاثر البيئي للري باستخدام المياه المعالجة وايجاد اية مخاطر تنتج عن ذلك ومحاولة التخفيف منها. تم اجراء هذه التجربة في بيت بلاستيكي ضمن ظروف متحكم بها في كلية الزراعة والطب البيطري– جامعة النجاح الوطنية – طولكرم, حيث تمت زراعة البذور خلال الموســـم الزراعي 2014/2013 في اوعية بلاســتيكية (6*6*7 ســم3) وتم اســتخدام رمل زراعي. وقد تم توزيع الاحواض بشــكل عشــوائي ثم تم ريها باســتخدام خمســة انواع مختلفة من المياه (المياه العادية وقد تم اســتخدامها كمرجع و المياه الناتجة من محطة التنقية, المياه الناتجة من محطة التنقية بعد ثلاثة سنوات, تسـع ســنوات , وخمســة عشــر ســنة) بمعدل ثلاث متكررات, وقد تم ملاحظة طول النبتة وعدد الاوراق خلال الزراعة. اســـتخدمت التحليلات الكيميائية لقياس محتوى كل جزء من اجزاء النبتة (التربة, الجذور و الاوراق) من العناصــر الثقيلة (Cd, Cu, Cr, Fe, K, Mn, Ni, Zn) باســتخدام جهاز ال ICP-MS. تم اســتخدام التحليل الاحصــائي لجميع البيانات التي تم جمعها خلال فترة الدراســة لدراســة تأثير المياه باســتخدام تحليل الانحدار الخطي حدود ثقة 95 % و تحليل الانحدار الخطي المتعدد , وايضـــا تم اســـتخدام AS/NZS ISO 31000: 2009 Risk Management – Principles and Guidelines لدراسة التقييم البيئي, اضافة الى استخدام عدة عوامل مثل: عمل الاغنـاء (Enrichment factor), عـامـل التراكم (Bioconcentration factor) و عـامـل الانتقال (Translocation factor).

اظهرت النتائج ان نوعية المياه لا تؤثر على طول النبتة في جميع العينات التي تم دراســـتها على العكس من عدد الاوراق التي نمت للنبتة حيث اظهرت الدراسة ان عدد الاوراق يتناقص مع استمرار الري باستـخدام المياه المعالجة لفترة زمنية طويلة. اظهرت النتائج ايضـا ان نوعية المياه تؤثر على قدرة اجزاء النبتة على امتصـــاص المعادن الثقيلة باســـتثناء معدن الزنك, حيث كان الامتصـــاص الاعلى لمعادن الكاديميوم, النحاس , البوتاسيوم, المنغنيز في اوراق الشعير المروية باستخدام المياه المعالجة اما بقية المعادن (الكروم, الحديد, النكيل و الرصاص) فكانت اعلى امتصاصا في التربة. وعند مقارنة النتائج بالحد الاعلى المسموح لتراكيز المعادن الثقيلة بالاوراق والجذور والتربة من قبل منظمة الصـحة العالمية ,كانت تراكيز الكاديميوم, الحديد, الرصـاص والزنك اعلى من الاحد الاعلى المسموح به في الاوراق , و تراكيز الكاديميوم, الحديد والرصـاص كانت اعلى من الحد المسموح به في الجذور. اما فيما يتعلق بالتربة فجميع المعادن كان تركيزها اقل من الحد الاعلى المســـموح به. اضافة الى ذلك تم استخدام عامل الاغناء(Enrichment Factor) لاحتساب نسبة تراكم المعادن الثقيلـة في الاوراق أو الجذور المرويـة بـالميـاه المعـالجـة الى تراكم المعـادن الثقيلـة في الاوراق او الجذور المروية بالمياه العادية (المرجع), وعامل التراكم (Bioconcentration Factor) لاحتساب نســبة المعادن المتراكمة في الاوراق او الجذور الى نســبة المعادن المتراكمة في التربة اضــافة الى عامل الانتقال (Translocation Factor) والذي يوضـــح كفاءة انتقال المعادن من الجذور الى الاوراق والقيمة التي تكون اكبر من 1 تعبر عن ان النبات يمكن اســـتخدامه لإزالة المعادن الخطرة من التربة, اظهرت النتائج ان معظم قيم عامل التراكم كانت > 1. لذلك مما ســـبق فان اجزاء نبتة الشـعير تتأثر بنوعية المياه التي يتم الري بها على المدى الطويل, واسـتمرار الري باسـتخدام المياه المعالجة ممكن ان يؤدي الى تراكم المعادن الثقيلة في اجزاء النبتة اعلى من الحد الاعلى المســموح به التي تم وضعها من خلال منظمة الصحة العالمية.

اضــافة الى ذلك فان نبتة الشـعير يمكن اسـتخدامها لإزالة بعض العناصـر الخطرة مثل الكاديميوم, النحاس, البوتاسيوم, المنغنيز والزنك. وهذه المياه المعالجة لا يمكن استخدامها كبديل لمياه الزراعة.