Al-Imam Muhammad Ibn Saud Islamic University

College of Science

Department of Chemistry

Detection, Quantification and Evaluation of Heavy Metals in Groundwater , Farm soils and plants Samples from some farms in Almuzahmiya, Riyadh Area

A graduation research project

submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

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VI. المستخلص:

تم جمع ستة عينات من المياه الجوفية و ستة عينات من التربة الزراعية و ستة عينات من سعف النخيل المزروع بستة مزارع بمنطقة المزاحمية بإمارة الرياض. تمت معالجة جميع العينات بالطر ق المناسبة لكل نوع من العينات كالتحميض والتجفيف والطحن ومن ثم تحليلها لفحص وتقدير العناصر السامة والثقيلة التالية : الحديد ، المنجنيز ، الخارصين، الكروم ، النيكل ، الكادميوم ، النحاس، الكوبالت و السيزيوم. الهدف من الدراسة الفحص والتقييم لاحتمال وجود مؤشرات للتلوث بالعناصر السامة والثقيلة في المياه الجوفية او تربة المزارع بمنطقة المزاحمية. خلصت الدراسة الى أن جميع عينات المياه الجوفية المستخدمة لري المزوعات بهذه المزارع خالية من مؤشرات التلوث بالعناصر السامة والثقيلة ، حيث أظهرت جميع الاختبارات ان تركيز العناصر تحت مستوى حد الإكتشاف لجهاز الحث البلازمي المزدوج المستخدم في تحليل العناصر. أظهرت التربة الزراعية بالمزارع مستويات عالية من الحديد كما هو متوقع في التربة الزراعية بأقل محتوى في تربة المزرعة رقم 3 (3403 ملغ / كلغ) وأعلى محتوى في المزرعة رقم 6 (21780 ملغ / كلغ) ، أما العناصر السامة والثقيلة الاخرى فقد كان تركيزها أقل من حد الااكتشاف للجهاز. أما في عينات سعف النخيل المزروع بهذه المزارع فلم تظهر تراكيز لكل العناصر السامة والثقيلة عدا عنصر الحديد حيث كان أعلى تركيز له في العينة رقم 1 (91.2 ملغ/ كلغ) وأقل تركيز في العينة رقم 4 (42 ملغ / كلغ) بمتوسط للعينات الستة بلغ 70 ملغ / كلغ .

أظهرت الدراسة تناسبا عكسيا بين محتوى الحديد في التربة الزراعية ومحتواه في سعف النخيل، فقد أظهرت الدراسة أن المحتوى العالي للحديد يوجد في عينات سعف النخيل المزروعة في المزارع التي يكون محتوى الحديد في تربتها منخفضا والعكس.

VII. Abstract:

Six samples of ground water, six samples of farm soils and six samples of date palms leaves were collected from some farms of Almuzahimiya area, Riyadh, Kingdom of Saudi Arabia.

The samples were analyzed for the following heavy and trace metal iron Fe, manganese Mn, zinc Zn, chromium Cr, nickel Ni, cadmium Cd, cobalt Co, copper Co and cesium Ce after suitable preparation and acidification. The study was carried to detect and evaluate the probability of any signs of pollution with trace and heavy metals in the irrigation ground water or farm soils. The study concluded to that the ground water used for irrigation of these farms was free from pollution with heavy metals where all the water

samples showed values below the detection limit of the ICP-OES instrument used for analysis. The farm soils samples contains high content of iron Fe as expected in any agricultural soil, with a minimum content in sample 3 (3403 mg/Kg) and maximum content in sample 6 (21780 mg/Kg) , all the farm soils were also free of other heavy and trace metals pollution. In the date palm leaves, no heavy and trace metals pollution was detected, except for iron Fe where a maximum value of 91.2 mg/Kg was detected in sample 1 and a minimum value of 42 mg / Kg was detected in sample 4, the average of the iron content in the six farm soils was found to be 70 mg/Kg. An inverse correlation was noticed between the iron content in the farm soil and the iron content in the date palm leaves grown in the farm, where the highest values of iron were found in the leaves of the date palms grown in relatively iron deficient soils.

CHAPTER ONE:

GENERAL INTRODUCTION

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1.1. Water resources in the Kingdom of Saudi Arabia (KSA):

The Kingdom of Saudi Arabia located in the continental region of the world in the semi-desert region, hence, the scarcity of permanent water resources, such as rivers and fresh water lakes, is an expected situation. Many other resources are available in the Kingdom and the national authorities are attempting to apply the perfect water resource management practices to it to satisfy the growing needs of the citizens to water for domestic uses , industry and agriculture. The main sources of water in the Kingdom are the following; Surface water which is the water collected during rainfall in the valleys and the artificial dams , constructed to collect the rain water for municipal and irrigation uses. Although this resource vary from season to another according to the rate of precipitation, the annual surface water is estimated to be about 2045 million cubic meters per year. The west and south-west regions of the Kingdom are the most rainy areas**[1].** **.** More than 237 dams, were built in the Kingdom to preserve the surface runoff water for groundwater recharge for different uses and to avoid flood emergencies near the valleys , the storage capacity of these dams is about 775 MCM **[2] .**

The second source is the desalinated seawater in which thermal evaporation and reverse osmosis technologies of salts removal from sea water is a promising way of providing a good quality water for municipal uses. The kingdom is the world largest producer of water from salt water and more than 35 desalination and power plants were constructed to provide about 1050 million cubic meters which satisfy more than 48 % of the domestic needs. The third resource is Reclaimed wastewater in which treatment and recycling of waste water is an important concept worldwide nowadays. recycling of purified sewage water for agricultural and industrial use is taking place and the first project in this respect was established in the city of Riyadh and saves about 200 000 m^3 of purified water a day. This recycled water is mainly used for irrigation of green yards and tree belts. For more than 1000 MCM a day of waste water, the water recycling emerge as a crucial need.

The fourth and the most important resource is the Groundwater where many aquifers in the Kingdom participate with about 1.5 million cubic meters per year, these aquifers have an average thickness of 500 meters present in the basement crystalline rocks. The surface aquifers are generally renewable depending on the amount of the rainfall, but the deep fossil water aquifers are nonrenewable and facing the problem of being depleting upon uncontrolled extraction especially in the agricultural areas where a growing demand arises. FAO in 2009 reported that the total ground water in the Kingdom estimates about 500 square kilometers, this report renders the ground water as an essential source of water in the kingdom **[3, 4].** The fossil water extracted from the artesian wells is usually used for irrigating agricultural crops, human consumption and drinking purposes, hence thousands of artesian and surface

wells have been drilled in the Kingdom.

1.2. Utilization of groundwater in agriculture in KSA:

Stress on water resources of the kingdom has been further multiplied due to agricultural development and has led to their partial depletion, particularly in the case of non-renewable ground and fossil water which is the main source of fresh water supplies. FAO (2009) reported that the desire to practice desert agriculture elevated the volume of water used for irrigation from about 6.8 km^3 in 1980 to about 21 km^3 in 2006. Further it was noticed that most of the water withdrawn came from fossil; deep aquifers. In the kingdom, some predictions or estimates are made on the presence of water resources that they may not last more than 25 years. Water is a scarce natural resource that ensures human, plant and animal life. This vital and essential resource needs to be managed in a manner that rationalizes its consumption and secures its supply for future generations.

1.3. Chemical constituents in the groundwater:

The Chemical constituents in the groundwater vary according to the geochemistry of the soil strata through which the groundwater percolates down to the aquifers. The geochemistry of inorganic minerals in the soil play an important role in the presence and amount of the major and trace chemical constituents in the groundwater. Fortunately, under many conditions existing in nature, many of the inorganic contaminants are not particularly mobile, and hence, the transport of inorganic contaminants frequently impeded naturally by the clays in the soil .

The inorganic constituents of groundwater can be divided broadly to major and trace components. Major inorganic constituents include metal ions like Ca, Mg, Na, K, Fe and Al in addition to anions such as carbonate $CO3^{-2}$, bicarbonates HCO_3^{-}, sulphates SO_4^{-2}, Phosphate PO_4^{-3}, chloride Cl^{-}, fluoride F^{-}, bromide Br^{-}, iodide I^{-}, silicates SiO_3^{-2}, ...etc. Trace metals and substances are those found in part per million (ppm) or part per billion (ppb) concentrations normally the term denoted to heavy metals and metalloids such as mercury Hg, lead Pb, chromium Cr, cadmium Cd, manganese Mn, arsenic As, selenium Se ......etc**. [5].**

1.4. Objectives of the study:

The primary objectives of this study are to detect and quantify the amount of the trace metals in 18 samples, 6 the groundwater, 6 soil and 6 date plant leaves of six farms in Almuzahmiya area and to correlate the presence and concentration of the trace and heavy metals in the irrigation ground water , agricultural soil and the leaves of the date palms trees grown in these farms.

CHAPTER TWO :

LITERATURE REVIEW

CHAPTER TWO :LITERATURE REVIEW

2.1. Water as a universal solvent:

Water has unique chemical properties in dissolving minerals and other substances due to its polarity and hydrogen bonds which means it is able to dissolve and hydrate metal ions, absorb, adsorb or suspend different compounds, thus, in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities. One of the most important environmental issues today is ground water contamination and between the wide diversity of contaminants affecting water resources, trace metals receive particular concern considering their strong toxicity even at low concentrations. They exist in water in colloidal, particulate and dissolved phases with their occurrence in water bodies being either of natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents). Some of the metals are essential to sustain life, like calcium, magnesium, potassium and sodium must be present for normal body functions. Water is an essential component of the environment and it sustains life on the earth. Human beings depend on water for their survival. Water is also a raw material for photosynthesis and therefore, is important for crop production. Obviously, an optimum agricultural production depends on water and soil quality[6]. Many other physical properties of water also play an important role in many natural phenomenea; such as, excellent solvent properties facilitates transport of nutrients and waste products, making biological processes possible in an aqueous medium. Highest dielectric constant of any common liquid results in high solubility of ionic substances and their ionization in solution. Higher surface tension than any other liquid which play an important role as controlling factor in physiology; governs drop and surface phenomena. Maximum density liquid at 4°C makes ice floats; and prevents vertical circulation restricted in stratified bodies of water. Higher heat of evaporation than any other material, determines transfer of heat and water molecules between the atmosphere and bodies of water. Higher latent heat of fusion than any other liquid except ammonia, temperature stabilized at the freezing point of water **[5].**

2.2. Ground water resources in KSA and geology:

Ground water is the water contained within cracks, fractures and pore spaces of soil, sediment and rocks beneath the surface of the earth . The groundwater flow path can be described as that, the atmospheric precipitation percolates into soil or bedrock directly or from surface lakes and streams, and generally flows downward under the force of gravity until it reaches some sort of physical barrier or impermeable zone, which either severely impedes flow or stops it altogether.

Ground water in Kingdom of Saudi Arabia is found in the area of the basement rocks and the thickness of these rocks could be about 500 m. Ground water is held in aquifers, some of which are naturally replenished, while others are non-renewable. In 1985, ground water provided 84% of the Kingdom's supply but it is noteworthy that most of this water was drawn from non-renewable aquifers. Similarly, the renewable groundwater resources were mainly stored in shallow alluvial aquifers and in basalt layers of varying thickness and width, and these aquifers mostly prevail in the southwest of the kingdom. They are in a position to store some 84 billion cubic metres with an average annual recharge of 1196 MCM. More than twenty layered principal and secondary aquifers of different geological ages store groundwater and the quality of the groundwater varies at various sites and aquifers. FAO (2009), maintains that total groundwater reserves (including fossil groundwater) have been estimated to 500 km^3. About 340 km^3 out of this 500 km3 is drawn at an extremely high rates . Estimates on available ground waters seem quite encouraging to meet the growing needs of the population of the kingdom **[3].**

Based on the isotopic analyses scientists believe that the fossil groundwater in these aquifers is ten to thirty-two thousand years old. At the depth of three hundred metres below ground surface about 2185 billion cubic metres groundwater is available with a total annual recharge of 2762 MCM **[2].**

2.3. Common minerals in the earth strata:

From a geochemical point of view, groundwater is important in the distribution and redistribution of chemical components, as it is a major terrestrial compartment in the water cycle and hence most biogeochemical cycles. Groundwater quality mapping is thus equally important for understanding the distribution and abundance of elements, and the changes in their global or local cycles due to the spreading of contaminants. **[7] .**

The major containments of ground and fossil water in KSA is found in the basement rocks and alluvial aquifers and in basalt layers, also more than twenty layered principal and secondary aquifers of different geological ages store groundwater and the quality of the groundwater varies at various sites and aquifers.**[2].** Water naturally contains number of different dissolved inorganic constituents. The major cations are sodium, potassium, cxalcium, magnesium and iron and the anions are chloride, sulphate , carbonate and bicarbonates. Potassium concentration in the groundwater come from many sources of potassium such as silicate minerals, orthoclase, microcline, hornblende, muscovite and biotite in igneous and metamorphic rocks and evaporate deposits, gypsum releases considerable amount of potassium, calcium and sulphate in to groundwater. Main reason increasing potassium into groundwater due to agricultural fertilizers. Fluorides come naturally into water by dissolving minerals that contain fluoride, such as fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$). Rocks rich in alkali metals have a larger content of fluoride than other volcanic rocks. Small amounts of fluoride are vital for the human organism, but it's toxic in larger amounts**[8].**

The WHO guideline value for fluoride in drinking water is 1.5 mg/l. Above 1.5 mg/l mottling of teeth may occur to an objectionable degree. Concentrations between 3 and 6 mg/l may cause skeletal fluorosis. Continued consumption of water with fluoride levels in excess of 10 mg/l can result in crippling fluorosis.

In many arid regions, drinking water is such a scarce commodity that governments have been forced to set the standard at higher levels, in order to have any drinking water at all. **[9].**

2.4. Reactions and solubility of earth minerals in ground water.

Groundwater is an important resource for human water supply and in Asia alone some one billion people are directly dependent on it. In Saudi Arabia, groundwater is the main source for safe and reliable drinking water consumption particularly in rural areas. Water taken from groundwater (wells) is often of better quality than surface water. This is true only if the soil or rock is fine-grained and does not have cracks, crevices and bedding plants, which permit free and faster passage of pollution such as of polluted surface water . The inorganic chemical quality of these waters is however, rarely adequately tested before the wells are put into production. Due to variation in the regional geology and water/ rock interactions, high concentrations of many chemical elements can occur in such water source. During the last 10 years several studies have shown that wells in areas with particular geological features yield water that does not meet established drinking water standards without any influence from anthropogenic contamination**[10].**

Variations in natural and human activities reflect spatial variations in the hydro-chemical parameters of the groundwater. The difference of dissolved ions concentration in groundwater are generally, governed by lithology, velocity and quantity of groundwater flow, nature of geochemical reactions, solubility of salts and human activities. Suitable quantity and quality of groundwater become a more crucial alternative resource to meet the drastic increase in social, agricultural and industrial development and to avoid the expected deterioration of groundwater quality due to heavy abstraction for miscellaneous uses. The main objective of this paper is to study the physical chemistry and bacterial contamination of groundwater of Rabigh government, Saudi Arabia. **[11].**

2.5. Groundwater pollution:

Groundwater chemistry is affected by both natural and anthropogenic processes. Natural processes include the types and rates of reaction between groundwater and minerals present in the rock, and the groundwater movement characteristics.

Anthropogenic processes usually involve the direct discharge of pollutants into the groundwater system. For example, the leaching of fertilizers may increase the nitrate levels in groundwater. In an urban environment, the hydrogeological system is usually complicated by numerous additional recharge sources, for examples leakage from water mains. Besides, urbanization could also modify the groundwater recharge mechanisms and the flow pattern. All these human induced processes may in turn affect the

groundwater chemistry. The impacts of the above components may differ from place to place depending on the level of urbanization.

Safe and good quality drinking water is essential for human health. However, when polluted, it may become a source of undesirable substances dangerous to human health. The main source of drinking water in Saudi Arabia is groundwater . Although, most regions in Saudi Arabia do not face serious problems regarding drinking water as other parts of the world, there are still water quality problems . There are several potential sources that may cause chemical and microbial contamination in groundwater. These include intensive application of organic and inorganic fertilizers, pesticides, and animal wastes . Seepage from septic tanks and wastewater discharged to soil might also in some locations contribute to the deterioration of both the chemical and the bacteriological quality of groundwater**[12].**

2.5.1. Anthropogenic groundwater pollution:

Many sources of anthropogenic activities threaten the quality of grounwater in many parts of the world. The main human activities than endangers the groundwater quality are the Industrial and Government Facilities and factories, the agricultrural activities such as fertilizers and pesticides, the sewage causes bacterial contamination, the mining and solid waste landfills and liquid effluent, petroleum industry... etc.

In China, more than 50% cities use groundwater as drinking water . But nitrate concentration in groundwater aquifers has steadily been increasing over the years mainly due to the extensive use of chemical fertilizers in intensive agriculture as well as discharge of domestic and animal wastes. At elevated concentrations, nitrate consumption causes methemoglobinemia in infants (Blue-Baby) and nitrate is reduced to nitrite in the intestine which has been said to be linked to several cancers. Furthermore, nitrosoamines are carcinogenic compounds that may be formed from nitrite in stomach. **[13].**

The pollution of groundwater is of major concern, firstly because of increasing utilization for human needs and secondly because of the ill effects of the increased industrial activity. The groundwater is believed to be comparatively much clean and free from pollution than surface water. Sodium and chloride occur naturally in groundwater. However, sources such as road salt storage and application, industrial wastes, sewage, fertilizers, water softener discharge, and proximity to saltwater are usually the cause of elevated levels in drinking water supplies. This can be a concern for people on low-sodium diets. Elevated levels of sodium and chloride can also interfere with taste, the watering of certain plants, and increase the corrosivity of water, which in turn can affect the household plumbing.

Anthropogenic activities like explosion of population, industrial growth, inputs of fertilizer, pesticides, and irrigation has been a crucial factor for determining the quality of groundwater.

Numerous publications have reported that urban development and agricultural activities directly or indirectly affect the groundwater quality

2.5.2. Natural groundwater pollution:

Salt water encroachment associated with over drafting of aquifers or natural leaching from natural occurring deposits are natural sources of groundwater pollution. Studies of variations in major ions help to identify the chemical processes and interaction between soil and water that are responsible for the changes in groundwater quality with respect to space and time. Many studies reported on the importance of groundwater recharge on seasonal variation in the major-ion concentration of groundwater ..

Groundwater chemistry, in turn, depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water rock interaction. Such factors and their interactions result in a complex groundwater quality**[14].**

2.6. Common inorganic ions in groundwater:

2.6.1. Cations:

The ions termed "major cations and anions" are: Na^{+} - sodium, Ca^{+2} - calcium , Mg^{+2} - magnesium, $NH4^{+}$ ammonium, K^{+} - potassium, Fe^{+2} and Fe^{+3} - iron, Mn^{+2} - manganese.

2.6.2. Anions:

SO_4^{-2} sulphate, Cl^{-} chloride, Alk - alkalinity (carbonate CO_3^{-2} plus bicarbonate HCO_3^{-}). Other species which are often included in the list for analysis and termed "minor cations and anions" are: NO_x - (nitrate plus nitrite), PO_4^{-3} phosphate, F^{-} fluoride and SiO_2 - silica.

2.7. Heavy metals in groundwater:

Early concerns over the quality of ground waters were focused mainly on dissolved mineral salts. However, recently, organics, heavy and trace metals have become a focus of concern for several reasons, including enhanced ability to detect chemicals in the microgram and nano gram per liter concentration levels and an increasing awareness of potentially hazardous risks to public health and the environment. Metals are ubiquitous, persistent and toxic at certain concentrations. Some metals are essential for heath whereas others have no known biological function and have toxic effects. The adverse effects of some metals on the human health are well documented. Trace elements are contributed to groundwater from a variety of natural and anthropogenic sources. Once liberated to groundwater, element distributions are continually modified by complex geochemical and biological processes .

Assessment of trace metals in ground water used for drinking purposes in Riyadh region in the kingdom of Saudi Arabia was carried out. Samples were collected from 200 wells supplying drinking water to the inhabitants in the region. All samples were analyzed for 17 trace and macro elements (Al, As, Ba, Be, Cd,Cr, Cu, Fe, Mn, Ni, Pb, Se, Mo, Ag, Hg,V and Zn) using Inductively Coupled Plasma (ICP) spectrophotometer equipped with an ultrasonic nebulizer**[15].**

3.8. Trace and heavy metals chemistry

These metal ions are generally relatively immobile under normal groundwater flow conditions. Low pH and/or EC cause the solubility of metals to increase. When low pH and/or EC develop, as is typical at a pollution site, trace metal concentrations can rapidly increase: i.e. the metals from the insoluble phase are mobilized. Then again, when the groundwater is brought to surface, CO_2 degassing and aeration occurs causing pH to rise and the Eh to tends towards oxidizing conditions causing the valence state of some of these metals to change to less soluble phases causing them to precipitate onto the sample bottle. In addition, when iron or manganese

precipitate, they are strong scavengers (adsorption) that will remove many metals from the solution by co-precipitation. From a health point of view, the important trace elements to guard against are cadmium, mercury, lead and arsenic (the dangerous four) since these have the most deleterious effects on humans. It is important to filter a sample for analysis as rapidly as possible after the groundwater has been brought to surface and with minimum exposure to the atmosphere. The filtered water is acidified to pH<2 to keep the metals in solution. Some laboratories request that the sample not be acidified in the field. These laboratories prefer to control the acidification in the laboratory, allowing sufficient time before analysis for any metals that may have precipitated to re-dissolve.

The sample bottles can be either plastic or glass. It is best to use new bottles as old bottles may have metals adhering to the sides. The bottles must be acid-rinsed in the laboratory to ensure that all leachable material has been removed. Analytical grade nitric acid must be added to the bottle before the filtered sample of groundwater is added. The acid can be added to the bottle either in the laboratory or in the field. If the bottle is pre-acidified then acid loss can occur if the bottle is either over-filled or rinsed out. In the field acid is added either by using ampoules (recommended) or by buretting (not recommended). The ampoules contain the correct amount of acid for the sample bottle. Their narrow necks with a cut groove are easy to break without spilling. After pouring out the acid, wash out the ampoule.

2.9. Ground water for agricultural purposes in KSA:

Stress on water resources of kingdom has been further multiplied due to agricultural development and has led to their partial depletion, particularly in the case of non-renewable fossil water which is the main source of fresh water supplies. **[3]** FAO (2009) reported that the desire to practice desert agriculture elevated the volume of water used for irrigation from about 6.8 km3 in 1980 to about 21 km3 in 2006. Further it was noticed that most of the water withdrawn came from fossil; deep aquifers.

In the kingdom, some predictions or estimates are made on the presence of water resources that they may not last more than 25 years. Water is a scarce natural resource that ensures human, plant and animal life. This vital and essential resource needs to be managed in a manner that rationalizes its consumption and secures its supply for future generations. The demand for water is increasing quite rapidly against the low and diminishing water resources. **[3] .**

Table 1: Growth of water use in Saudi Arabia, 1980 - 2010 in millions cubic meters

Year	Domestic and Industrial sectors (MCM)	%	Agricultural sector (MCM)	%	Total
1980	502	21.3	1850	78.7	2352
1990	1650	6.06	25 589	93.94	27 239
1992	1870	5.9	29 826	94.1	31 696

1997	2063	11.17	16 406	88.83	18 469
2000	2900	20.57	11 200	79.43	14 100
2010	3600	19.67	14 700	80.33	18 300

2.10. Contamination of agricultural soil with polluted irrigation water:

Water is an essential component of the environment and it sustains life on the earth. Human beings depend on water for their survival. Water is also a raw material for photosynthesis and therefore, is important for crop production. Obviously, an optimum agricultural production depends on water and soil quality . Diffuse agricultural pollution results from the excess application of fertilizer and manure. Apart from enhanced nitrogen concentrations, it also results in elevated concentrations of salt, potassium and phosphorous. Furthermore, magnesium and calcium are often applied to agricultural fields for optimal pH and base cation conditions . Indirect effects of manure application, resulting from its acid load, are an increase
in hardness of groundwater[7].

2.11. Absorption of heavy metals by cultivated plants:

The role of heavy and trace elements in the soil system is increasingly becoming an issue of global concern at private as well as governmental levels, especially as soil constitutes a crucial component of rural and urban environments , and can be considered as a very important “ecological crossroad” in the landscape . Agricultural soil contamination with heavy metals through the repeated use of untreated or poorly treated wastewater from industrial establishments and application of chemical fertilizers and pesticides is one of the most severe ecological problems in Bangladesh. Although some trace elements are essential in plant nutrition, plants growing in the close vicinity of industrial areas display increased concentration of heavy metals, serving in many cases as biomonitors of pollution loads . Vegetables cultivated in soils polluted with toxic and heavy metals take up such metals and accumulate them in their edible and non-edible parts in quantities high enough to cause clinical problems both to animals and human beings consuming these metal-rich plants as there is no good mechanism for their elimination from the human body . Toxic metals are known to have serious health implications, including carcinogenesis induced tumor promotion, and hence the growing consciousness about the health risks associated with environmental chemicals has brought a major shift in global concern towards prevention of heavy metal accumulation in soil, water and vegetables .

Heavy metals and trace elements are also a matter of concern due to their non biodegradable nature and long biological half-lives. Wastewater from industries or other sources carries appreciable amounts of toxic heavy metals such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil which create a problem for safe rational utilization of agricultural soil . Long-term use of industrial or municipal wastewater in irrigation is known to have a significant contribution to the content of trace and heavy elements such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil . As a result, excessive accumulation of trace elements in agricultural soils through wastewater irrigation may not only result in soil contamination but also affect food quality and safety **[16].**

Pollution of the natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms, when permissible concentration levels are exceeded. Heavy metals frequently reported in literature with regards to potential hazards and occurrences in contaminated soils are Cd, Cr, Pb, Zn, Fe and Cu . Soil samples represent an excellent media to monitor heavy metal pollution because anthropogenic heavy metals are usually deposited in top soils . Heavy metal contaminated soil affects the ecosystem when heavy metals migrate into groundwater or are taken up by flora and fauna, this results in great risk to ecosystems due to bioaccumulation **.** Vegetables cultivated in soils polluted with toxic and heavy metals take up such metals and accumulate them in their edible and non-edible parts in quantities high enough to cause clinical problems both to animals and human beings consuming these metal-rich plants as there is no good mechanism for their

elimination from the human body . Heavy metals and trace elements are also a matter of concern due to their non-biodegradable nature and long biological half-lives. Pollution of the natural environment by heavy metal is a worldwide problem because these metals are indestructible and most of them have toxic effects**[17].**

CHAPTER THREE :MATERIALS AND METHODS

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3.1. Study Area: Six ground water samples (GW), 6 farm soil samples (FS) and 6 date palm leaves samples (DPL) were collected from six farms located in Al-Muzahmiya area, 50 kilometers west of Riyadh city. The sampling was carried in February 2015 .The sampled farms were of private property and used for date palms plantation.

3.2. Collection of Samples:

6 ground water samples were collected in four-liter plastic bottles, which were previously washed with tap water and rinsed with distilled water and then two more times with the water sample . The sample bottles were completely filled and closed perfectly. All samples were transported to the laboratory and the PH and conductivity were measured. The samples were kept to be analyzed for the other tests in the shortest possible time **[18].**

Six composite soil samples, each of about 2 kilograms mass, were collected from different places in the prescribed farms. The agricultural soil was collected from depths in the range between 5 to 30 cm , ten subsamples were collected from each farm to make one composite sample in a plastic bag. The samples were cleaned from course aggregate and plants stems and crushed to pass 2 mm sieve, then quartered and kept in a 200 grams plastic bottles for further analysis.

The six date palm leaves were collected from date palms trees planted in the farms under study , dried in the shadow for 3 days and then cut with stainless scissor to small pieces and kept in a plastic container for further analysis.

Table 2: names of farms and sample numbers:

Farm number	Farm name	Groundwater samples (GW..)	Farm Soil samples (FS..)	Date palm leaves samples (DPL ..)
1	Abu Mohammad	GW 1	S1	DPL1
2	Aalim Al- Rashidi	GW 2	S2	DPL2
3	Khalid Mousa	GW 3	S3	DPL3

4	Abu Khalid	GW 4	S4	DPL4
5	Saeid Al- Gahtani	GW 5	S5	DPL5
6	Ali Al- Gahtani	GW 6	S6	DPL6

3.3. Samples preparation:

3.3.1. Ground water samples:

500 ml of each sample were taken as laboratory samples. the PH and conductivity were measured and recorded .The water (pH) was determined using a pH meter (pH meter - Adwa, model AD8000, PH/mV/EC/TDS/Temp.), after calibration with standard buffer 4.01 and 7.0, the results are shown in table **(3).** The electrical conductivity (EC) was determined using a conducti- meter - model Adwa, model AD8000, PH/mV/EC/TDS/Temp.) , after calibration with standard potassium chloride solution, the results are shown in table **(3),** then the samples were acidified with 2 M nitric acid to PH of about 2 and kept in a clean plastic container for heavy and trace metal analysis.

3.3.2. Farm Soil samples:

About 5 grams of each soil sample were weighed accurately on an analytical balance in a 200 ml clean beaker, 25 ml of concentrated hydrochloric and nitric acid (3:1) mixture were added then the mixture was boiled on the hot plate in the fume hood for 20 minutes to complete the elements extraction, the mixture was cooled and filtered through Whatman no. 1 filter paper in a 100 ml volumetric flask, the soil residue and the filter paper were washed several times with hot distilled water and the volume was completed to the mark, stoppered and shaken.

3.3.3. Preparation of date palm leaves samples:

About 5 grams of each leaves sample were weighed accurately in a dry clean porcelain crucible. The crucible and samples were ignited gently on a Bunsen flame till most of the carboneous material was burned. The crucible and content were transferred to a muffle furnace at 550 ^{0}C and left for four hours. The crucibles were allowed to cool and the ash percent was determined as in table 4, and dissolved in a 20 ml of 1:1 hydrochloric acid and boiled for 2 minutes to complete the extraction. The cold extract was filtered in a 100 ml volumetric flask, the insoluble residue and the filter paper were washed several times with hot distilled water and completed to the mark and kept for further analysis.

3.4. Trace metals analysis:

Standard mixture of the following elements Fe, Mn, Zn, Cr, Co, Ni, Ce, Cu and Cd was prepared for the construction of the standard calibration curves for each element. The Inductively Coupled Plasma - Optical Emission Spectroscopy instrument (ICP-OES) was used for the analysis using argon as a plasma gas after suitable dilution for certain samples. The trace metal content of the ground water samples was shown in table 5, that of farm soil was shown in table 6 and the trace metals content of the date palms leaves was shown in table 7.Check standards were analyzed routinely during the analysis and R of more than 0.999 was maintained for the calibration curve and analysis.

CHAPTER FOUR :

RESULTS AND DISCUSSION

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The physical properties of the ground water were determined, as in table 3, all the samples PH fall within the limits of drinking water standards (6.5 - 8.5) . The maximum PH was found in sample 1(8.06) and the lowest in sample 2 (6.67), with an average PH of 7.89, hence the ground water can be considered as suitable water for irrigation of plants. The electric conductivity EC, is very high in all samples , with an average of 1760 ms this can be attributed to the high ionic salts content found in ground water due to the dissolution from the mineral found in the soil strata. The temperature of the samples did not vary from the normal temperature of the surrounding with an average of 23.37 ^{0}C.

Table 3: Physical properties of the groundwater samples:

Sample number	PH-value	Conductivity in ms	Temperature ^{0}C
GW1	8.06	1543	23.3
GW2	7.67	1444	23.3
GW3	7.97	1995	23.4
GW4	7.83	1854	23.4
GW5	7.95	1906	23.4
GW6	7.85	1855	23.4
average	**7.89**	**1760**	**23,37**

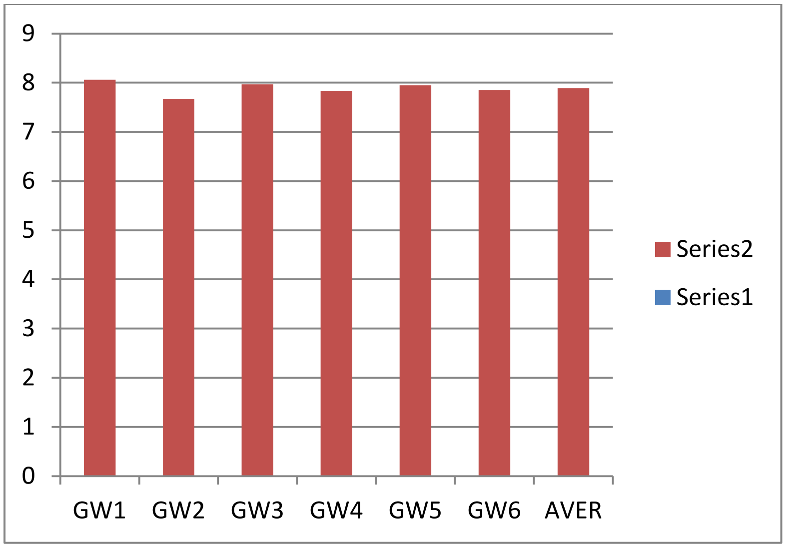

Fig. 1: The PH of the ground water samples.

The ash content of the date palms leaves samples was determined using the ignition method . The average ash content of the samples was found to be 7.71 %, with a maximum ash percent in sample 5 of 9.87%. and a minimum ash in sample 3 (6.16%). The ash content give an indication to the metal content of the sample and consequently as a sign of pollution with major and trace metals. The results are shown in table 4.

Table 4: Ash percent of the date palm leaves samples.

Sample number	Weight of sample g	Weight of ash g	Ash percent
DPL1	5.0823	0.3985	7.84%
DPL2	5.0145	0.4518	9.01%
DPL3	5.0204	0.3092	6.16%
DPL4	5.2904	0.3491	6.60%
DPL5	5.0509	0.4983	9.87%
DPL6	5.2556	0.3567	6.79%
average	**5.1190**	**0.3939**	**7.71%**

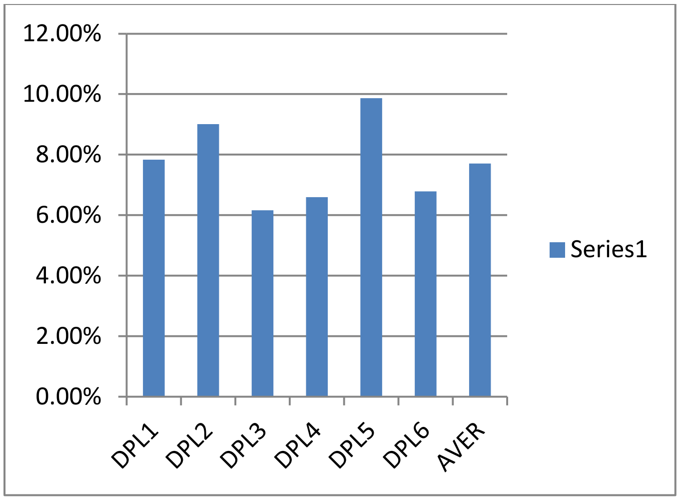

Fig. 2: The ash percent of the date palms leaves samples.

The trace metal content in the ground water samples was found below the detection limit of the ICP- OES instrument for each element. This indicates that the six samples under study are all free of trace metals contamination neither natural nor anthropogenic rendering the ground water suitable for irrigation of plants and vegetables, without any ambiguities of contaminating the agricultural soil in the farms. The results are shown in table 5.

Table 5: Results of trace metals in ground water (GW) samples.

Sample	Fe	Mn	Zn	Cr	Co	Ni	Ce	Cu	Cd
GW1	< 0.001	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
GW2	< 0.001	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
GW3	< 0.001	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
GW4	< 0.001	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
GW5	< 0.001	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
GW6	< 0.001	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005

The analysis of farms soil showed that no signs of heavy and toxic metals pollution in the agricultural soil of all elements except iron Fe. High iron contents appeared in all soil samples acid extract of maximum content in sample 6 with 21780 mg/Kg and a minimum content in sample 3 of 3403 mg/Kg. this high content is due to the natural occurrence of iron minerals in Almuzahmiya soils. The absence of iron in the ground water samples indicates that it is immobile and sparingly soluble in the ground water or the soluble part of the iron in the ground water has been adsorbed and retained by the different clay minerals and rocks in the soil. The results are shown in table 6.

Table 6: Results of trace metals in farms soil (FS) samples in mg/kg.

Sample	Fe	Mn	Zn	Cr	Co	Ni	Ce	Cu	Cd
FS1	5304	< -1.702	< -2.032	< 0.002	< 0.009	< -2.169	< -1.972	< 0.003	< 0.005
FS2	4020	< -1.960	< -2.263	< 0.002	< 0.009	< -2.198	< -2.028	< 0.003	< 0.005
FS3	3403	< -2.050	< -2.310	< 0.002	< 0.009	< -2.218	< -2.047	< 0.003	< 0.005
FS4	17640	< -2.117	< -2.332	< 0.002	< 0.009	< -2.236	< -1.988	< 0.003	< 0.005
FS5	12580	< -2.214	< -2.348	< 0.002	< 0.009	< -2.235	< -1.960	< 0.003	< 0.005
FS6	21780	< -2.024	< -2.299	< 0.002	< 0.009	< -2.214	< -1.943	< 0.003	< 0.005

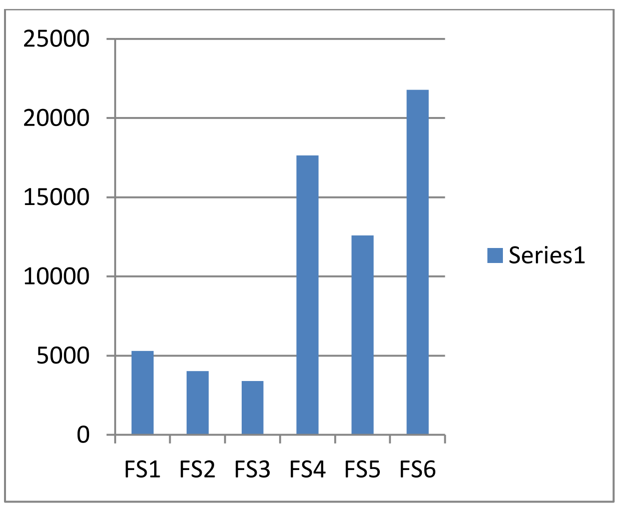

Fig. 3: The iron content of the farm soils samples in mg / Kg.

The plant absorb the water and elements from the soil, fortunately no signs of Zn, Cr, Co, Ni, Ce , Cu and Cd metal pollution were shown in the leaves of the date palms cultivated in Almuzahmiya farms and are all found below the detection limit of the instrument. Manganese was also found below the detection limit in all samples except for sample 2 where 11 mg/Kg content was detected . Iron, Fe, which cannot be considered as a toxic element, the average iron Fe content was found to be 70 mg/Kg in the leaves with maximum and minimum content of 91.2 and 42 mg/ Kg in sample 1 and 4 respectively. The results are shown in table 7.

Table 7: Results of trace metals in date palm leaves (DPL) samples in mg/kg.

Sample	Fe	Mn	Zn	Cr	Co	Ni	Ce	Cu	Cd
DPL1	**91.2**	< 0.001	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
DPL2	**88.0**	**11.00**	< 0.002	< 0.002	< 0.009	< 0.013	< 0.004	< 0.003	< 0.005
DPL3	**79.6**	< -0.155	< -0.979	< 0.002	< 0.009	< -2.093	< -1.866	< 0.003	< 0.005
DPL4	**42.0**	< -0.146	< -1.339	< 0.002	< 0.009	< -2.130	< -1.908	< 0.003	< 0.005
DPL5	**69.0**	< -1.286	< -1.254	< 0.002	< 0.009	< -2.096	< -1.875	< 0.003	< 0.005
DPL6	**42.8**	< -1.320	< -1.395	< 0.002	< 0.009	< -2.194	< -1.972	< 0.003	< 0.005

An inverse correlation was noticed in the iron content of the date palms leaves and the iron content of farm soil. The highest iron contents was recorded in DPL1, DPL2 and DPL3 where the content of Fe was 91.2, 88 and 79.6 mg/Kg , the farm soils from which the leaves were brought showed a lowest iron content as follows; 5304, 4020 and 3403 mg/Kg respectively. The farm soils with high iron content like FS4, FS5 and FS6 showed the lowest iron content as in DPL4, DPL5 and DPL6 of 42, 69 and 42.8 mg/Kg respectively.

5. Summary and Conclusion:

Six samples of ground water, six samples of farm soils and six samples of date palms leaves were collected from some farms of Almuzahimiya area, Riyadh, Kingdom of Saudi Arabia. The study was carried to detect and evaluate the probability of any signs of pollution with trace and heavy metals in the irrigation ground water or farm soils. The samples were analyzed for the following heavy and trace metal iron Fe, manganese Mn, zinc Zn, chromium Cr, nickel Ni, cadmium Cd, cobalt Co, copper Co and cesium Ce after suitable preparation and acidification.

The physical properties of the ground water samples such as PH and conductivity were determined and then the samples were acidified to PH= 2 for trace and heavy metals analysis Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument after preparation of suitable calibration curves for the elements under study.

The farm soil samples were dried in the shadow for three days, crushed, sieved and quartered. The heavy and trace metals content was extracted by aqua - regia, filtered and diluted to 100 ml volumetric flask for elemental analysis with ICP-OES.

The dates palm leaves were dried, cut to small pieces and ashed in Bunsen flame and at 600 ^{0}C in the muffle furnace for 4 hours, the ash percent was determined. The elemental content of the ash was determined by ICP-OES after dissolution in dilute hydrochloric acid, filtered and diluted to 100 ml in a volumetric flask .

The study concluded to that the ground water used for irrigation of these farms was free from pollution with heavy metals where all the water samples showed values below the detection limit of the ICP-OES instrument used for analysis. The farm soils are also not polluted with toxic metals, but considerable content of iron was noticed. The date palms leaves are also free of toxic metal contamination except iron Fe, where appreciable concentrations were detected in the ash of the leaves.

6. Recommendations:

The study recommend continuous monitoring of the ground water, farms soil and the plants contents of heavy and trace metals to insure good quality of the agricultural products from these farms. The reversible correlation of the iron content in the date palms leaves and the farm soil iron Fe content need further studies to confirm it.

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