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Impact of Leachate on Soil and Groundwater Quality in Vicinity of Landfill Sites of Kirkuk City (Kirkuk-Iraq)

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A B S T R A C T

Leachate, soil and groundwater samples were collected from the zindana, Alwasit (1) and Alwasit (2) landfill sites in Kirkuk city (North- Iraq), to study the possible impact of leachate percolation on soil and groundwater quality. Various physicochemical parameters and heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Fe and Zn) were determined in leachate, soil and water samples to assess metal contamination due to landfill wastes. Soil contamination is assessed on the basis of Enrichment Factor, Contamination Factor and Pollution Load Index were estimated for some selected potentially hazardous elements (Zn, Pb, Cd, Sr, Ni, Mn, Cr). The results for EF values were within moderate enrichment category due to anthropogenic activity and for CF was low to moderate degree of contamination. The result of (PLI) of the three landfill sites of soil samples indicates that the soil at Kirkuk landfill sites is under load of pollution due to contaminants arising from landfill leachates. A human health risk assessment model adopted by the USEPA demonstrated for the soil and groundwater samples for the three main pathways that Human beings may expose to metals, Non-carcinogenic health effects (HQs) and the cumulative hazard quotient index (HI) for both children and adults were calculated for Mn, Ni, Pb, Sr, Zn, and Cd suggesting no health hazards for now, yet the influence of leachates may cause serious toxic risk to the soil and groundwater quality in the distant future.

Introduction

Kirkuk city is located in the north of Iraq governorate, about 236 km away from the capital Baghdad. It is one of the rich-oil provinces in Middle East. According to the Kirkuk municipality, Kirkuk city has a population of about 1000000 inhabitants resides in a number of quarters, this

scattered distribution of population causes disseminated generation of solid wastes; and consequential environmental degradation. More than 90% of the Municipal Solid Waste (MSW) generated in city was directly dumped on land in an uncontrolled open-dumps generating several point sources of

contamination. Therefore the state of the city suggested to built a sustained Solid Waste landfill site, the Program was initiated in 2005 and was completed in 2008. This site represents the first environmentally engineered and constructed landfill in Iraq. Kirkuk landfill have two solid waste transfer stations to provide added capacity and to compact the trash before being transferred to the landfill (Sameer, *et al*, 2013). The precipitation that falls into a landfill, coupled with any disposed liquid waste, results in the extraction of water containing innumerable organic and inorganic compounds is called 'leachate'. This leachate accumulates at the bottom of the landfill and are gradually released into the surrounding environment over a period of years and causes large amounts of hazardous and otherwise deleterious chemicals to reach nearby groundwater, surface water and soil also to the air, via leachate and landfill gas. Increasing waste generation and disposal resulted in increase soil and ground water pollution. Various physicochemical parameters including heavy metals were analyzed in the leachate, soil and groundwater samples via to estimate the toxicity of these metals both in soil and ground water and characterize the potential health risks on both adults and children and evaluate the most significant contaminant and exposure pathway with regard to human health. The objective of the study therefore was to assess the effect of landfill pollution on groundwater quality in Kirkuk city.

Materials and methods

The Study Area

The zindana, Alwasit (1) and Alwasit (2) landfill Sites are situated around Kirkuk city (North-Iraq) between latitudes ($35^{\circ} 22' 12''$ - $35^{\circ} 30' 36''$) North, and longitude ($44^{\circ} 22' 12''$ - $44^{\circ} 24' 36''$) East, (Fig-1). Kirkuk city

is the head quarters of Kirkuk District which sprawls over 20000 km² with population of around 1000000 inhabitants. Generally it is characterized with moderate rainfall (from Oct-April) with an average annual rainfall reaches (275mm) and the average annual temperature is ranged between ($9-36^{\circ}\text{C}$). Two of the landfill sites (Alwasit -1 and Alwasit -2) are dump sites, one at east of Kirkuk city (2.5km from the municipality boundary) and the second site located at the north of city (9 km from the municipality boundary) respectively and they are operating as points of waste accumulation all over the city to be transported to the main landfill site called (zindana landfill site) situated in Zindana village about 18 km from the southern peripheral of Kirkuk city. It started in operation in the year 2008, covering an area about approximately (193) Km², surrounded by commercial, industrial and residential set-ups. The solid waste in Kirkuk city has a big quantity of more than 1000 tons per day (Brian, E.C. McCarty. (2008b)) and consists of everyday items such as food scraps, product packaging, grass clippings, furniture, clothing, bottles, paint and batteries. It does not include medical that have been treated separately.

Geology of the area

Kirkuk city is surrounded from North and north east side by Kirkuk anticline, and from south west side by Jambur anticline while the Khasa seasonal river pass through its center.

The area is covered by sedimentary rocks from the oldest Tertiary (AL-fatha, Injana, Muqdadiya, and bai-Hassan formations) to the Recent (Pleistocene and Holocene) Quaternary deposits. These sediments are composed mainly of sandstones, siltstone, clay stone, gravel, sand and shell.

Hydrologically, the main aquifer at area is unconfined, located within Quaternary deposits, the movement of ground water is in the direction of the topographic slope of the area (East and Southeast toward West and Northwest of the area). The depth of groundwater table in Kirkuk city varies from 6 to 45 m with respect to ground level.

Sampling of leachate, soil and groundwater

Leachate samples were taken on 10th July 2015 from the slump pond in the center and around the landfill site in order to study their contaminants concentrations. The Samples were collected using new 2L Polyethylene bottles washed with distilled water. At the sampling site, the bottles were rinsed three times with the leachate to be sampled prior to filling and labeled. Water quality in terms of parameters pH, Electrical Conductivity (EC), Total Dissolved solid(TDS), Total Suspended Solid (TSS), Biological Oxygen Demand(BOD₅), Chemical Oxygen Demand(COD), Chloride(Cl⁻), Sulphate (SO₄⁻²), Phosphate(PO₄⁻³), Nitrate (NO₃⁻) and Nitrite (NO₂⁻) were carried out using the Standard Methods for the Examination of Water and Wastewater (APHA, 2003).The pH, EC and TDS were recorded in the site at the time of sampling field with portable digital pH, EC, and TDS meter (HI 9813-6). For the analysis of biological oxygen demand (BOD₅), 300 ml capacity BOD bottles were used according to Azide modification of Winkler method. Leachate and groundwater samples were extracted for heavy metals using hydrochloric acid as digestion reagent and analyzed by atomic absorption spectrophotometer (AAS) (PYE UNICAM Model SP 191). In an effort to assess the groundwater contamination in the area, (16) ground water samples were collected from specific tube wells. The sampling points was kept to be nearest to landfill sites. Figure. 1

For ground water sample collection, 2 L Polyethylene sampling bottles were used, which were rinsed 2-3 times with the sample water which was to be collected. To prevent the loss of certain cations sampling bottles were acidified with diluted HCl.

Laboratory analysis The chemical analysis was done in accordance with the APHA methods. The pH, EC and TDS was measured using conductivity meter; Sodium and potassium by Flame photometer; Calcium, Magnesium and Chlorine by Titration method; COD by Open reflux digestion method & titration; BOD by Winkler method; Sulphate, Phosphate and Iron by Spectrophotometer and Heavy metals (Cr, Cu, Zn, Ni) by Atomic Absorption Spectrometer.

In July 2015, a total number of 5 surface (10–20cm) soil samples were collected within the area nearby to the landfill sites. The samples were collected in self-locking polythene bags and were sealed in double bags.

Chemical analyses for the water and soil samples were performed at the accredited Acme Analytical Laboratories of Canada. Incorporation of replicates, reagent blanks and reference materials provided by the ACME Analytical Laboratories validated the excellent accuracy and precision of analytical results.

Results and Discussion

Leachate characteristics

Physicochemical characteristics of the leachate samples collected from the three landfill sites are presented in TABLE 1.

Physicochemical characteristics of the leachate depend primarily upon the waste composition and water content of total

waste. TDS values are ranged between (1400-2450 mg/l) and that high values of TDS indicates the presence of inorganic material in the samples. Values of EC which is observed are varied from 3150 to 28500 $\mu\text{S}/\text{cm}$ recorded from the three sites and reflects the presence of anions and cations or inorganic materials (Kale *et al.*, 2010). The ratio of BOD₅/COD values of 0.41, 0.37, 0.42, were observed for leachate samples, respectively. This ratio provides a good estimate of the state of the leachate, as the ratio for young leachate is generally between 0.4-0.5 (Kurniawan *et al.*, 2006). The leachate is characterized by high levels of BOD₅ and COD which tends to indicate the maturity of the landfill and shows that microbial activity in the decomposing leachate is yet to attain stability. The PH values of studied leachate samples are less than 7.0 except in sample S3 and this variety in pH value may be attributed to the type of biological decomposition of the wastes and to the dilution effects and the efficiency of the leachate treatment system (Kjeldsen, *et al.*, 2002). A high concentration of Chloride was also observed in the leachate samples (480-5398 mg/l).

Table(2) shows Heavy metals contents of the leachate samples obtained from laboratory analysis include (Lead(Pb), Nickel(Ni), Iron(Fe), Zinc(Zn) and Cadmium (Cd)). The high level of Fe (8.1 mg/L) in the leachate sample indicates that iron and steel scrap are also dumped in the landfill at a larger quantity (Bendz, 1997). The presence of Zn (2.3-8.0 mg/L) in the leachate shows that the landfill receives waste from batteries and fluorescent lamps. The presence of Pb (1.10 mg/L) was also detected in the leachate samples but the concentration was comparatively lower. Ni (0.02-1.7 mg/L), Cd (0.006-1.7 mg/L) were also present in the leachate samples. A variety of waste is dumped at the landfill sites, indicating the

origin of these heavy metals in leachate (Christensen *et al.*, 1994).

Physico-chemical Characteristics of the Soil

The result of soil texture analysis showed that the soil is of sandy silt type (Folk, 1974) as it consisted of mixture of silt, sand, and clay with average percentages of (65.6%, 20.4 % and 13.9%) respectively. The highest and lowest average organic carbon (O.C) content are 1.269%-0.34% respectively, Soil pH varies between 7.73 and 8.02. showing pH variations are subtle and only slightly vary in the alkaline range.

Total contents of heavy metal in the topsoil of the study area are presented in Table 3. The average abundance order of heavy metal contents in the soil samples are:- (Mn>Sr>Cr>Ni>Zn>pb>Al>Cd). The maximum determined concentrations of Mn, Sr, Cr, Ni, Zn, Pb, Al, and Cd are 577.4, 499.9, 182.8, 107.8, 103, 26.6, 7.24 and 0.33 mg/kg, respectively. The increase in the heavy metals concentration near the landfill sites probably reflects the role of leachate contamination and soil type.

In order to assess the level of contamination and for a better estimation of anthropogenic input into soil, the Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI) were estimated for some selected potentially hazardous elements (Zn, pb, Cd, Sr, Ni, Mn, Cr) evaluated in this study.

EF is a powerful tool to distinguish between anthropogenic and naturally occurring sources of heavy metals (Jafaru *et al.*, 2015). This factor was initially developed to speculate on the origin of elements in the atmosphere, precipitation, or seawater, but it was progressively extended to the study of

soils, lake sediments, peat, tailings, and other environmental materials. The following equation was used to calculate the EF (Zakir *et al*, 2008).

$$EF = (C_m/CAI)_{\text{sample}} / (C_m/CAI)_{\text{Earth's crust}} \dots\dots\dots 1-1$$

Where, $(C_m/CAI)_{\text{sample}}$ is the ratio of concentration of element (C_m) to that of Al (CAI) in the soil or sediment sample and $(C_m/CAI)_{\text{Earth's crust}}$ is the same reference ratio in the earth's crust. Al was selected as the reference element, due to its crustal dominance and its high immobility (Jafaru *et at*.,2015). The reference value of Al is 7.8% (Zakir, 2008).The world average elemental concentrations reported by (Kabata, 2007) in the Earth's crust were used as reference in this study because regional geochemical background values for these elements are not available. Five contamination categories are recognized on the basis of the enrichment factor: $EF < 2$ states deficiency to minimal enrichment; $2 \leq EF < 5$, moderate enrichment; $5 \leq EF < 20$, significant enrichment; $20 \leq EF < 40$, very high enrichment; and $EF > 40$, extremely high enrichment (Zakir, 2008).

Mean EF values of elements in the soil samples were followed the order $Cd > Ni > Pb > Zn > Sr > Cr > Mn$. Values of EF for soil are listed in Appendix (A). EF value for elements (Pb,Zn,Cd, Mn, Cr) in soil were less than 2 which are within deficiency to minimal enrichment, indicating that these elements in the surface soil are originated predominantly from predominantly from the crustal materials of natural origin. (Jafaru *et at*,2015). while all other EF values were within moderate enrichment category due to anthropogenic activity.

The contamination factor (CF) is used to classify the level of contamination of metals in the soil samples by dividing the

concentration of each metal in the soil or sediments by the baseline or background value (Jafaru *et at*,2015). Contamination factor is calculated as:

$$CF = (C_m)_{\text{Sample}} / (C_m)_{\text{Background}} \dots\dots\dots 1.2$$

Where, $(C_m)_{\text{Sample}}$ is the concentration of a given metal in soil, and $(C_m)_{\text{Background}}$ is meaning background contents of trace elements in continental crust. The following terminologies are used to describe the contamination factor: $CF < 1$, low contamination factor; $1 \leq CF < 3$, moderate contamination factors; $3 \leq CF < 6$, considerable contamination factors; and $CF \geq 6$, very high contamination factor (Hakanson, 1980).

Mean CF values of elements in the surface soil were followed the order $Cd > Ni > Pb > Zn > Sr > Cr > Mn$. Values of CF in soil are listed in Appendix (B). Range and mean of CF values for elements in soil are listed in Appendix (B). CF value for elements (Pb,Zn,Sr,Ni, Cr) in soil were in moderate contamination factors range and low degree of contamination, while CF values of Cd shows considerable contamination factor and (moderate degree of contamination) suggesting the anthropogenic activities caused by leachate contaminants as the main source.

Pollution load index (PLI)

The PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. The $PLI > 1$ is polluted; whereas < 1 indicates no pollution (Abed,2015). This parameter is expressed as:

$$PLI = (CF_1 * CF_2 * CF_3 * \dots * CF_n)^{1/n} \dots\dots\dots 1.3$$

Where, n is the number of metals.

PLI values of the three landfill sites of soil samples were > 1, indicating that the soil at Kirkuk landfill sites is under load of pollution due to contaminants arising from landfill leachates. (Figure 2).

Health Risk Assessment Model

Human health risk assessment calculations were based on the assumption that residents, both children and adults, are directly exposed to soil through three main pathways (a) Ingestion of soil occurs by eating soil particles and/or licking contact surfaces (e.g., hands) and It is assumed that children present a higher ingestion rate, due to hand-to-mouth intake.; (b) dermal absorption through exposed skin and (c) inhalation of soil particles (<10 μm)present in the air both by mouth and nose during breathing (USEPA, 1989). Equations (1.4), (1.5) and (1.6) were used to estimate the Chronic Daily Intake of each exposure route considered (USEPA, 1996; USEPA, 2002). The variables used in equations below are listed in Appendix (C).

$$CDI_{ing} = C_{soil} * \frac{IngR * EF * E}{BW * AT} * CF \dots\dots 1.4$$

$$CDI_{drm} = C_{soil} * \frac{SA * SAF * DA * EF * ED}{BW * AT} * CF \dots\dots 1.5$$

$$CDI_{inh} = C_{soil} * \frac{InhR * EF * ED}{PEF * BW * AT} \dots\dots\dots 1.6$$

The carcinogenic and non-carcinogenic side effects for each trace elements were computed individually, as toxicity calculation uses different computational methods. For each trace element and pathway, the non-cancer toxic risk was estimated by computing the Hazard Quotient (HQ, also known as non-cancer risk-

Equation (1.7) for systemic toxicity (USEPA, 2004). If HQ exceeds (1), it indicates that non- carcinogenic effects might occur.

To estimate the overall developing hazard of non-carcinogenic effects, it is assumed that toxic risks have additive effects. Therefore, it is possible to calculate the cumulative non-carcinogenic hazard index (HI), which corresponds to the sum of HQ for each pathway (Equation 1.8) (USEPA, 1998). Values of HI < 1 indicate that there is no significant risk of non-carcinogenic effects. While, values of HI > 1 imply that there is a probability of occurrence of non-carcinogenic effects, and are enhanced with increasing HI values (USEPA, 2004).

$$HQ = \dots\dots\dots 1.7$$

$$HI = \Sigma HQ = HQ_{ing} + HQ_{drm} + HQ_{inh} \dots\dots\dots 1.8$$

HQing values in soil of the study area for elements Cr, Mn, Ni, Pb, Sr., Zn,Al,and Cd, were less than (1) for children and adults, indicating no hazards (Figure 3A). However, HQing values of Cr, and Al were 0.925 and 0.779 respectively, may act as a trigger for a future health risks specially with continuous adding of these elements through anthropogenic activities and with long term exposure. Through comparison between values of HQing for adults and children, we deduce that children are more susceptible to adverse health effects than adults (Figure.3A).

Values of HQdrm of elements in the studied soil were much less than (1) for both children and adults, suggesting no health hazards through dermal exposure, although adults are more susceptible to dermal exposure pathway than children (Figure 3B).

HQinh values of elements in the soil were much less than (1) (Appendix D), for both children and adults, suggesting no health hazards (Figure 3C).

HI values of elements were less than (1) for both children and adults, suggesting no hazards (Figure 3D) (Appendix D). Through comparison among the three exposure pathways (i.e. ingestion, dermal and inhalation), ingestion pathway had more serious effects on health than others, while inhalation exposure had the less effects.

For carcinogens, the Lifetime Average Daily Dose (LADD) used in the assessment of cancer risk for trace elements has been calculated for each exposure route as shown in Eq. (1.9).

Calculation of the lifetime average daily dose for carcinogens (USEPA,2004) :

$$LADD = \frac{C \cdot EF}{AT} * \left(\frac{CR_{child} \cdot ED_{child}}{BW_{child}} + \frac{CR_{child} \cdot ED_{child}}{BW_{child}} \right) \dots\dots\dots 1.9$$

Where the variables C, EF, AT, ED, and BW are mentioned in (Appendix D) except: CR is the contact (or absorption) rate (i.e. ingestion [CR = IngR], inhalation [CR = InhR] and dermal absorption [CR = SA x SAF x DA] rates).

The risk due to the cancerous effects is determined by multiplying the life time average daily dose (LADD) with the corresponding slope factor of the exposure path and then the risk for each exposure path is summed up to get the overall cancer risk (Khairy *et al.*, 2007).

$$Risk = LADD * SF \dots\dots\dots 1.10$$

Where Risk is cancer risk; SF is cancer slope factor of contaminants, where SF of As by ingestion, dermal and inhalation is

1.5, 3.66 and 15.1 mg/ kg/day respectively; SFinh (slope factor by inhalation) of Cd, Cr, Co, and Ni are 6.3, 9.8, 42, and 0.84 (mg/kg)/day respectively, while SFing (slope factor by ingestion) of Pb is 0.0085 (mg/kg/day)-1 (USEPA,2004).

Carcinogenic hazards from carcinogen elements (i.e. Cd, Cr, Ni, and Pb) in soil samples were listed in (Appendix C and D). Cancer risk between (10-6) and (10-4) indicated potential health risk according to (USEPA, 1998), while greater than (10-4) suggests high potential health risk (USEPA, 2005).

Values of cancer risk for elements in the surface soil via three exposure pathways (i.e. ingestion, dermal and inhalation) were in the order Cr >Ni >Cd >Pb. Cancer risk values for Cd and Pb in soil were 3.3*10-7 and 3.8*10-7 respectively (Appendix D) which refer to no hazard via inhalation and ingestion of these two elements. Carcinogenic risk of Ni via inhalation exposure was (1.4*10-5), suggesting a moderate potential health risk, While Cr had a cancer risk (1.2*10-3) via inhalation exposure, indicating high potential health risk.

Groundwater quality

The groundwater of the study area is mainly used for domestic and irrigation purposes, Therefore it is important to evaluate the suitability of groundwater for that purposes as Geochemical data corroborates the effects of the landfill leachate on groundwater Appendix (E).

The ionic composition of groundwater from wells near the landfill is represented by the Piper trilinear diagram (Piper, [22]) (Figure 4) The plot indicates that most of the groundwater samples represent MgSO4 type

of water. Some samples fall in the field of mixed Ca-Mg-Cl. Very few samples represent NaCl and mixed Ca-Na-HCO₃ facies.

The average pH value of water (7.34) was found to be alkaline in nature and within the permissible level of WHO (WHO, 2011). The E.C of water is reflection of the quantity of ionic constituents dissolved in it. and its value ranges between 1219-5100 μ S/cm for groundwater samples this value is higher than the recommended standard by WHO and I.Q.S for drinking water. Highest value was well closed to landfill sites, which is a strong indication of contaminant through it. The Total Dissolved Solids (TDS) value ranges from 597 to 2499 mg/l, high values near dumpsites and tends to decrease with distance of groundwater wells from the dumpsite, along groundwater flow paths in down gradient direction. The values of TDS for monitoring wells were within the permissible limit of WHO except for those near the dumpsites which have high levels indicating the effect of leachate on ground water especially during wet periods.. The existence of high concentration values of some principal ions (K, Na, Cl and SO₄), and heavy metals (Cr, Ni, Co, Mo and Sr), especially in the southeastern sector of the investigated area along the flowing direction. These values exceed the limits for the drinkableness of the water.

All groundwater samples were analyzed for heavy metals The Results are tabulated in Appendix(F). Most of these heavy metals have low concentrations and they are within the permissible limits for drinking water standards (WHO, 2011) except metals such as Br, Fe, Cr, Sr, Ni and Pb, which are characterized with certain degree of toxicity metals in drinking water. among these metals Bromide(Br) has the maximum concentration of (589ppb) at (W1) comes

from wastes associated with excessive usage of fertilizers and other chemicals, Higher concentration of Iron(Fe) in some water samples (W1, W7, W5) shows the influence of leachate on groundwater sources near the landfill sites. lead, zinc and chromium metals which indicated presence of toxic wastes perhaps from disposed off of battery cells, chemicals used for photograph processing, Pb-based paints and pipes and steel scraps into the landfill sites. As the maximum concentrations of these metals was (50), (1821) and (47.8) parts per billion.

***generally ;The extent of contamination level of groundwater quality due to leachate percolation depends upon a number of factors like chemical composition of leachate, rainfall, depth and distance of the well from the pollution source (the landfill site in the present case). Groundwater samples of different depths and distances from landfill sites were analyzed in the present study to understand the level of combination (Mor *et al.* [4]). From the analysis, it is evident that the concentrations of contaminants were found to be high in the sampling sites which are near to the landfills. Interestingly, the groundwater contamination drops fast with increase in the distance of sampling sites from the landfill sites. The percolation of leachate was further found to become gentler. However, this aspect needs further investigations by drilling more wells of varying depths for having a proper correlation between distance and percolation depth.

Although, the concentrations of few contaminants did not exceed drinking water standard even then the groundwater quality represent a significant threat to public health. Strictly speaking one should avoid using groundwater drawn from the wells located in proximity of the waste dumping sites. If this is unavoidable, deeper drilling

and frequent analysis of water samples are desirable.

Health Risk Assessment Model

Risk assessment method is used to evaluate the actual or potential adverse effects of contaminants to residents living, animals and plants in the studied area and surrounding villages and which concentrate on the damage that has been or will be done by contaminants (Kelepertzis, 2014). Human beings may expose to metals through three main pathways including direct ingestion, inhalation through mouth and nose, and dermal absorption through skin exposures; ingestion and dermal absorption are common for water exposure. The numeric expressions for risk assessment were obtained from the USEPA Risk Assessment Guidance for Superfund (RAGS) methodology. The dose received through the individual pathway considered was determined using Equations (1.11) and (1.12) from the US Environmental Protection Agency (USEPA, 2010).

$$ADD_{ing} = \frac{CW \cdot IR \cdot EF \cdot ED}{(BW \cdot AT)} \dots\dots\dots 1.11$$

$$ADD_{drm} = \frac{CW \cdot SA \cdot Kp \cdot ET \cdot EF \cdot ED \cdot CF}{BW \cdot AT} \dots\dots\dots 1.12$$

Where: ADD is an Average Daily Dose by ingestion (ADD_{ing}) and dermal absorption (ADD_{drm}), unit in µg/kg/day; BW is Average Body Weight (kg, 70 for adults and 15 for children); EF is Exposure Frequency(days/year, 350); ED is Exposure Duration (years, 70 for adults and 6 for children); IR is Ingestion Rate (l/day, 2.2 for adults and 1.8 for children); Cw is concentration of the estimated metal in water (µg/l); SA is exposed Skin Area (cm², 18000 for adults and 6600 for children); Kp is dermal permeability coefficient in water (cm/h); ET is Exposure Time (h/day, 0.85

for adults and 1 for children); AT is Averaging Time (days, for non-carcinogenic ED * 365); CF is unit Conversion Factor (l/cm³, 0.001). Risk characterization was quantified by non-carcinogenic risks. Potential non-carcinogenic risks, reflected by the Hazard Quotient (HQ), were evaluated by comparing exposure or average intake of contaminants from each exposure route (ingestion, dermal) with the corresponding reference dose (RfD) using Equation (1.13).

$$HQ = \frac{ADD}{RfD} \dots\dots\dots 1.13$$

Where: HQ is Hazard Quotient via ingestion or dermal contact (unit less); RfD is Reference Dose via Ingestion or Dermal in (µg/kg/day) (USEPA, 2013, 2005; Kelepertzis, 2014). If HQ exceeds 1.0, there is unacceptable risk of adverse non-carcinogenic effects on health, while if HQ < 1.0, it is an acceptable level of risk (Kelepertzis, 2014). To estimate the total potential non-carcinogenic risks posed by more than one pathway, the Hazard Index (HI) was introduced, which was the sum of the HQs from all applicable pathways (Σ HQ_{ing} + HQ_{drm}). HI >1 indicated a potential for an adverse effect on human health or the necessity for further study (USEPA, 2004). If the HI value is less than unity, non-cancer risks are not expected to occur from any chemical. If the screening level HI exceeds one, there may be concern for potential non-cancer effects and some follow-up evaluation is needed, with the probability increasing as the value of HI increases (USEPA, 1998).

Values of HQ_{ing} (hazard quotient by ingestion) for the water samples are summarized in Appendix(F)..and are illustrated in fig (5A). Were the values for

trace elements As, B, Ba, Cr, Co, Fe, Mn, Sr, U, V, Zn, and Mo, except Br, Ni, and Pb were smaller than (1) for child, suggesting that these elements posed no hazard (Figure 5A). HQing value of Br is 1.578, implying causes adverse health effects for children and potential non-carcinogenic concern. Though, HQing value of arsenic is less than (1) (Fig 5B), but still may consider a trigger for future health effects especially when children subject to long term exposure with continuous adding of arsenic through anthropogenic activity. Values of HQing of adult were less than (1) for all trace elements except for (Br, Ni) suggesting no adverse health effects. Through comparison between values of HQing for adults and children, we deduce that children are more susceptible to adverse health effects than adults.

Values of HQ_{derm} all elements were much less than (1) (Fig 5B) for both adults and children implying no hazards. Dermal exposure pathway has no effects on health in comparison with ingestion exposure pathway.

HI values for children for all elements were less than (1) (Fig 5C), except Br, Ni, and Pb which had a values of (6.3, 8.109, and 3.209) respectively, suggesting health hazards. HI values for adults were much less than (1) indicating no hazards caused by ingestion and dermal exposure, but still Br, and Ni elements had a values of HI > 1.0 (1.478, 2.333) respectively showing adverse health effects and potential non-carcinogenic concerns, and Pb element has a value of (0.853), which may act as a trigger for future health effects on adults and child especially with continuous adding of Pb element through anthropogenic activities. Children are more susceptible to potential health effects than adults.

Conclusion

The present study has shown that the impacts of the leachates from landfill sites in Kirkuk city cannot be neglected. THE study primarily indicated that Kirkuk landfill sites cumulatively generates significant amount of leachate which contains high TDS value due to the presence of inorganic material in the samples whereas high levels of BOD₅ and COD. The high BOD and COD values indicate the high organic strength in the leachate of all landfill sites and the ratio of BOD₅/COD values indicates that the leachate is young and shows that microbial activity in the decomposing leachate is yet to attain stability. Heavy metals contents of the leachate samples include high level of Pb, Ni, Fe, Zn and Cd were the variety of waste is dumped at the landfill sites, indicates the origin of these heavy metals in leachate.

The soil and groundwater samples around all these landfills is also contaminated having heavy metals and other cations and anions more than recommended by IQS and WHO standards for drinking water. The concentration of all these heavy metals shows possible leaching of contaminant from landfill.

The analyzed soil samples obtained from the vicinity of the landfill dump site were mostly of sandy silt type. The average abundance order of heavy metal contents in the soil samples are (Mn > Sr > Cr > Ni > Zn > Pb > Al > Cd). Soil contamination is assessed on the basis of the Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI) were estimated for some selected potentially hazardous elements (Zn, Pb, Cd, Sr, Ni, Mn, Cr) evaluated in this study. EF value for elements (Pb, Zn, Cd, Mn, Cr) in soil were less than (2) which are within deficiency to minimal enrichment, indicating that these elements in

the surface soil are originated predominantly from predominantly from the crustal materials of natural origin while for (NI and Sr) EF values were within moderate enrichment category due to anthropogenic activity.

The application of contamination factor (CF) with background values for elements (Pb,Zn,Sr,Ni,Cr) shows moderate contamination factors range and low degree of contamination,while CF values of Cd reveals considerable contamination factor and (moderate degree of contamination) suggesting the anthropogenic activities caused by leachate contaminants as the main source. The result of Pollution load index (PLI) of the three landfill sites of soil samples were > 1, indicating that the soil at Kirkuk landfill sites is under load of

pollution due to contaminants arising from landfill leachates.

A human health risk assessment model adopted by the USEPA demonstrated that for the soil for the three main pathways that Human beings may expose to metals including direct ingestion, inhalation through mouth and nose, and dermal absorption through skin exposures; the calculated non-carcinogenic health effects (HQs) and the cumulative hazard quotient index (HI) for both children and adults were less than (1) for Mn, Ni, Pb, Sr, Zn, and Cd suggesting no health hazards, while Ni and Cr metals may act as a trigger for a future health risks specially with continuous adding of these elements through anthropogenic activities and with long term exposure.

Table.1 Physicochemical concentration in leachate sample

| leachates sample | Turbidity NTU | PH | TDS PPM | Conductivity $\mu\text{s}/\text{cm}$ | T.H ppm | Ca.H ppm | Mg.H ppm | HCO ₃ -ppm | COD ppm | BOD ppm |
|------------------|---------------|------|---------|--------------------------------------|---------|----------|----------|-----------------------|---------|---------|
| L1 | --- | 6.83 | 1543.5 | 3150 | 10334 | 706 | 328 | 1340 | 851 | 352 |
| L2 | --- | 6.96 | 2415.7 | 4093 | 1400 | 1030 | 370 | 423 | 891 | 994 |
| L3 | --- | 8.35 | 13965 | 28500 | 1360 | 480 | 880 | 7420 | 994 | 371 |

Table.2 Heavy metals concentration in leachate sample

| Surface Water sample | Cl ppm | Fe ppm | NO ₃ ppm | SO ₄ ⁻² ppm | Pb ppm | Zn ppm | K ppm | Cd ppm | Ni Ppm |
|----------------------|--------|--------|---------------------|-----------------------------------|--------|--------|-------|--------|--------|
| L1 | 352 | 0.364 | 3.1 | 322 | 0.012 | 0.12 | 128.2 | 0.006 | 0.038 |
| L2 | 770 | 1.5 | 2.67 | 133 | 49.5 | 8.0 | 113.5 | 0.009 | 0.022 |
| L3 | 5398 | 8.1 | ----- | 76 | 8.45 | 2.3 | 1554 | 0.022 | 1.7 |

Fig.1 Kirkuk landfill site

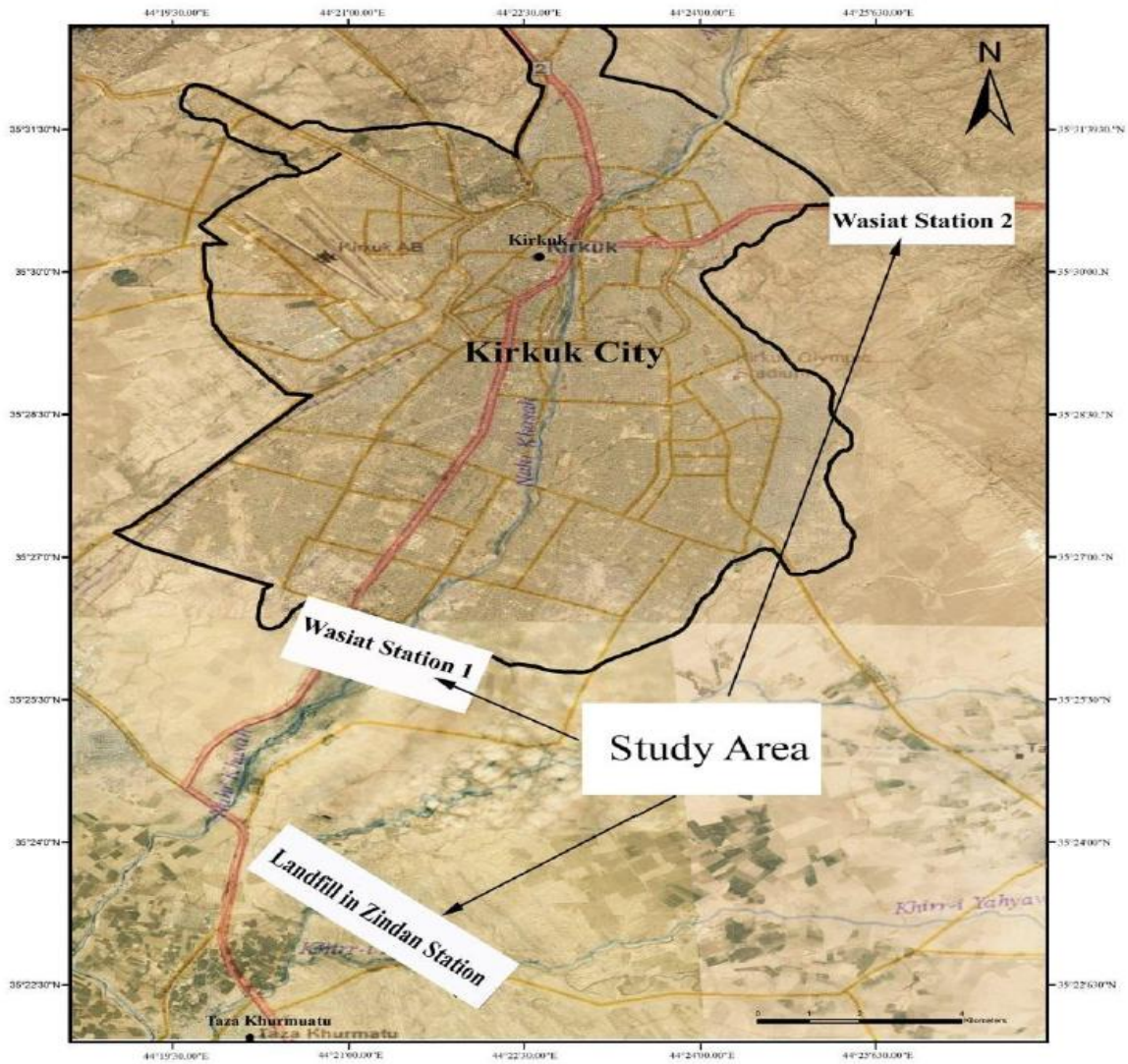


Fig.2 values of Pollution load index in the Soil of Study

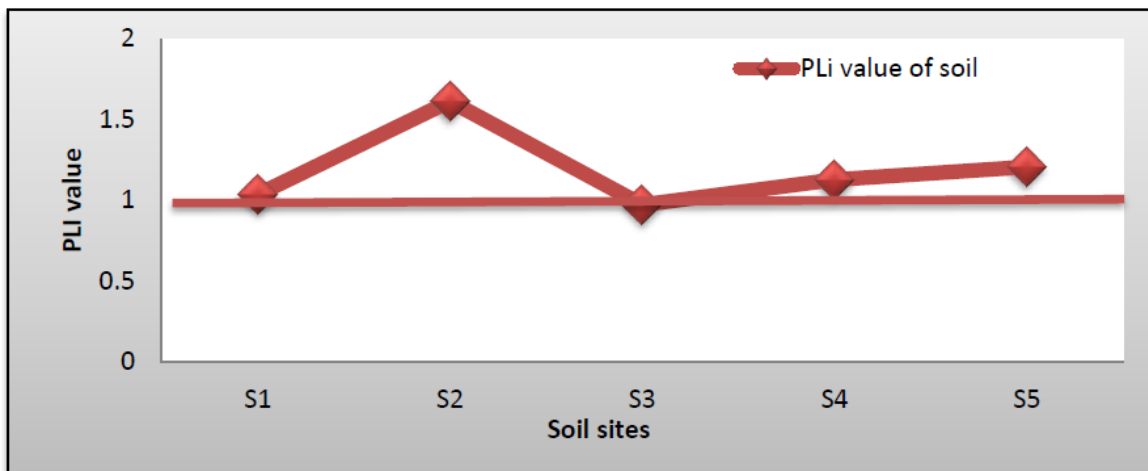


Fig.3 HQing shows the values of (A), HQdrm (B), HQinh (C) of the soil study area

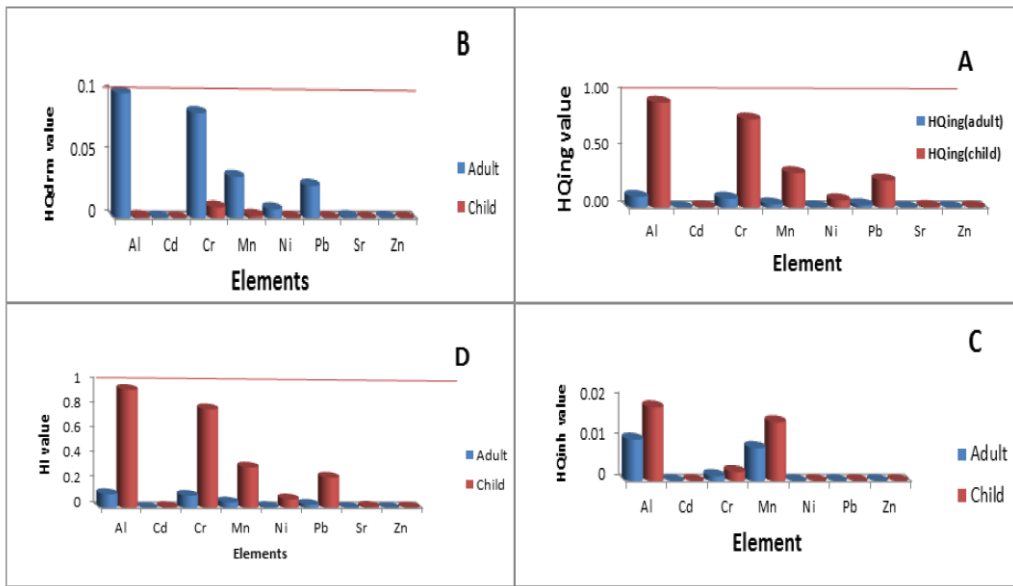


Fig.4 Piper rating models for water during the dry season

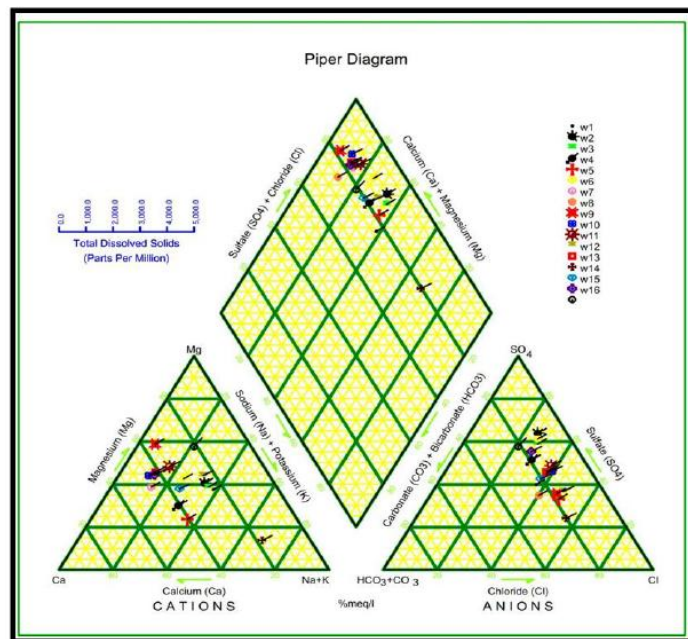
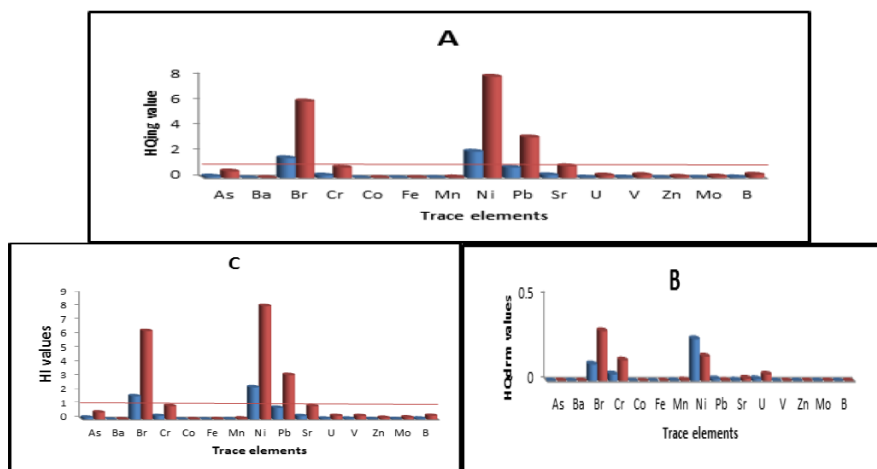


Fig.5 Shows HQing values, HQdrms (B), HI (C) in the groundwater for children



Carcinogenic hazards from carcinogen elements (i.e. Cd, Cr, Ni, and Pb) in soil samples has been calculated for each exposure pathway route and their Values were in the order Cr > Ni > Cd > Pb. Cancer risk values for Cd and Pb in soil refer to no hazard while for Cr and Ni via inhalation exposure was (1.2×10^{-3}) and (1.4×10^{-5}) respectively, suggesting a moderate to high potential health risk.

The groundwater of the study area is mainly used for domestic and irrigation purposes. Geochemical data reflect water quality that is affected by the leachates collected from the refuse landfill site.

The groundwater samples around all these landfills is also contaminated having heavy metals and other cations and anions more than recommended by IQS and WHO standard for drinking water and this is may be due to the migration of leachate into soil and groundwater especially during rainy seasons when the leachat pond is filled and seeps and accumulates in the surface drainage. All groundwater samples were analyzed for heavy metals were most of them have low concentrations and they are within the permissible limits for drinking water standards (WHO, 2011) except metals

such as Br, Fe, Cr, Sr, Ni and Pb, which are characterized with certain degree of toxicity metals in drinking water. among these metals Bromide (Br) has the maximum concentration of (589ppb) at (W1) comes from wastes associated with excessive usage of fertilizers and other chemicals, Higher concentration of Iron (Fe) in some water samples (W1, W7, W5) shows the influence of leachate on groundwater sources near the landfill sites. lead, zinc and chromium metals which indicated presence of toxic wastes perhaps from disposed off of battery cells, chemicals used for photograph processing, Pb-based paints and pipes and steel.

The risk assessment for oral exposure of inhabitants in the area indicated that the non-carcinogenic risk tends to become significant for children and adults with long term exposure duration. mainly for Br, Ni, and Pb exposure since their values exceeded the acceptable limits of non-cancer hazard quotient. The cumulative hazard quotient index (THI) of the study area indicated a serious potential health hazard which Br, Ni, and Pb were apparently the main critical factors. finally The groundwater sample analysis result clearly indicated that the trend of reducing contaminant

concentration at increasing radial distances away from the landfill site for all contaminants studied.

Nevertheless the influence of leachates on the groundwater quality may cause serious toxic risk to the soil and groundwater quality in the distant future.

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Appendix (A): The values of Enrichment factor for Trace Elements in the Soil of Study Area.

| Trace Element | EF value of surface soil | EF category |
|----------------------|---------------------------------|---|
| Pb | 1.98 | deficiency to minimal enrichment |
| Zn | 1.74 | deficiency to minimal enrichment |
| Cd | 4.5 | Moderate enrichment |
| Sr | 1.488 | Moderate enrichment |
| Ni | 2.12 | moderate enrichment |
| Mn | 0.889 | deficiency to minimal enrichment |
| Cr | 1.482 | deficiency to minimal enrichment |

Appendix (B): The values of contamination factor for Trace Elements in the Soil of Study Area.

| Trace Element | CF value of soil | CF category |
|----------------------|-------------------------|---|
| Pb | 1.81 | moderate contamination factor |
| Zn | 1.584 | contamination factors moderate |
| Cd | 3.3 | considerable contamination factors |
| Sr | 1.349 | moderate contamination factor |
| Ni | 1.925 | moderate contamination factor |
| Mn | 0.806 | low contamination factor |
| Cr | 1.344 | moderate contamination factor |

Appendix (C): Variables for Estimation of Soil Risk in the Soil of Study Area.

| Parameter | Meaning | Valve | | Reference |
|--------------------------------|--|--|-------|---|
| | | Child | Adult | |
| AT _c (day) | Averaging time for carcinogenic effects | LT*365 | | (USEPA, 2001) |
| AT _{dc} (day) | Averaging time for non carcinogenic effects | ED*365 | | (USEPA,2001) |
| BW(kg) | Average body weight | 15 | 70 | (Catherine et al, 2007.USEPA1989) |
| C _{sod} (mg/kg) | concentration of the element in soil,or totle Bap-equivalent concentration for carcinogenic PAHs | | | |
| CF | conversion factor | | | |
| DA (unitless) | Dermal absorption factor | 0.03 for As; 0.001 for other elements ;0.13 for PAHS | | USEPA 2002 |
| CDI _{ing} (mg/kg/day) | Chronic daily intake dose through ingestion | | | Eq. 5.3 |
| CDI _{drm} (mg/kg/day) | Chronic daily intake through dermal contact | | | Eq. 6.3 |
| CDI _{hm} (mg/kg/day) | Chronic daily intake through inhalation | | | E.q.7.3 |
| ED (year) | Exposure duration | 6 | 30 | (USEPA, 2001) |
| EF (day/year) | Exposure frequency | 350 | | (USEPA, 2001) |
| IngR(mg/day) | Soil ingestion rate | 200 | 100 | (USEPA, 2001) |
| InhR(M3/day) | Inhalation rate | 7.6 | 20 | Catherine et al, 2007 |
| PEF (M3/kg) | Particle emission factor | 1.36* 10 ⁹ | | (USEPA, 2001) |
| SA(Cm2) | Exposed skin area | 2800 | 5700 | (USEPA, 2001) |
| SAF(gm/cm2) | skin adherence factor | 0.2 | 0.07 | (USEPA, 2001) |
| RfD _{ing} (mg/kg/day) | Chronic Oral reference dose | | | (USEPA, 2013;Ferreira - Baptista 2005) |
| RfD _{drm} (mg/kg/day) | Chronic dermal reference dose | | | (Ferreira -Baptista 2005 ;Li 2010) |
| RfD _{hm} (mg/kg/day) | Chronic inhalation reference dose | | | (Huang et al ,2014 ;Ferreira -Baptista 2005) |

Appendix (D): Hazard Quotient and Hazard Index for Trace Elements in the Groundwater of Study Area.

| Element | RfD _{ing} | RfD _{drm} | HQ _{ing} | | HQ _{drm} | | HI=∑HQs | |
|---------|--------------------|--------------------|-------------------|--------|-----------------------|-----------------------|---------|-------|
| | μg/kg/day | μg/kg/day | Adult | child | Adult | child | Adult | child |
| As | 0.3 | 0.285 | 0.140 | 0.536 | 6.67*10 ⁻⁴ | 1.96*10 ⁻³ | 0.141 | 0.538 |
| B | 200 | 180 | 0.072 | 0.2786 | 3.84*10 ⁻⁴ | 0.001 | 0.073 | 0.280 |
| Ba | 200 | 14 | 0.005 | 0.020 | 3.67*10 ⁻⁴ | 1.08*10 ⁻³ | 0.006 | 0.022 |
| Br | 4 | 0.3 | 1.578 | 6.025 | 0.099 | 0.294 | 1.478 | 6.320 |
| Cr | 3 | 0.075 | 0.220 | 0.840 | 0.041 | 0.123 | 0.262 | 0.946 |
| Co | 0.3 | 0.06 | 0.064 | 0.024 | 1.52*10 ⁻⁴ | 0.0001 | 0.007 | 0.025 |
| Fe | 700 | 140 | 0.0084 | 0.0320 | 1.9*10 ⁻⁴ | 1.79*10 ⁻⁴ | 0.009 | 0.033 |
| Mn | 24 | 0.96 | 0.187 | 0.0714 | 0.0022 | 0.0065 | 0.021 | 0.078 |
| Mo | 5 | 1.9 | 0.0382 | 0.0112 | 3.50*10 ⁻⁴ | 0.001033 | 0.033 | 0.012 |
| Ni | 20 | 0.8 | 2.085 | 7.962 | 0.247 | 0.1459 | 2.333 | 8.109 |
| Pb | 1.4 | 0.42 | 0.839 | 3.2054 | 0.0132 | 0.003917 | 0.853 | 3.209 |
| Sr | 600 | 120 | 0.2467 | 0.9421 | 5.85*10 ⁻³ | 0.01727 | 0.253 | 0.959 |
| U | 3 | 0.06 | 0.0583 | 0.2228 | 0.0138 | 0.04086 | 0.072 | 0.264 |
| V | 5 | 0.13 | 0.0678 | 0.259 | 3.22*10 ⁻⁵ | 9.50*10 ⁻⁴ | 0.068 | 0.260 |
| Zn | 300 | 60 | 0.0315 | 0.120 | 7.47*10 ⁻⁵ | 0.00132 | 0.032 | 0.122 |

Appendix(E). presents the analytical results of the groundwater samples and the comparison with World Health Organization standard (WHO,2011) and (IQS2009).

| Major& Miner ions | Wet season | | Dry season | | IQS,2009 (ppm) | WHO,2011 (ppm) |
|-------------------------------|-------------|------------|--------------|------------|----------------|----------------|
| | Range (ppm) | Mean (ppm) | Range (ppm) | Mean (ppm) | | |
| PH | 8.35-6.7 | 7.382 | 8.16-6.93 | 7.34 | 6.5-8.5 | 6.5-8.5 |
| Turbidity NTU | 35.8-0.79 | 12.973 | 17.7-0.51 | 3.11 | 5.0 | 5.0 |
| TDS (ppm) | 2499-597 | 1152.47 | 2136.4-605.1 | 967.46 | 1000 | 1000 |
| EC μ /cm | 5100-1219 | 2260.25 | 4360-1235 | 2097.8 | ----- | ----- |
| T.H as CaCO ₃ ppm | 770-45 | 518.87 | 246-1760 | 884.7 | 500 | 500 |
| Ca ²⁺ | 42-209 | 144 | 106.9-399.3 | 192.98 | 150.0 | 100.0 |
| Mg ²⁺ | 24-136 | 87.834 | 117.3-323.3 | 232.09 | 100.0 | 125.0 |
| Na ⁺ | 28.9-526 | 228.925 | 38-504 | 183.10 | 200 | 200 |
| K ⁺ | 1.6-10.5 | 4.147 | 1.28-3.05 | 1.83 | ----- | 12.0 |
| Cl ⁻ | 85-475 | 262 | 329-548 | 429.43 | 350.0 | 250.0 |
| SO ₄ ²⁻ | 470-925 | 598 | 354-1838 | 705.62 | 400.0 | 250.0 |
| HCO ₃ ⁻ | 115-400 | 230.5 | 250-500 | 343.68 | ----- | ----- |
| NO ₃ ⁻ | 5.96-76 | 35.62 | 5.8- | 33.65 | 50.0 | 50.0 |

Appendix(F) :It shows the concentrations of ions archaeological elements of groundwater models and compare them with the Iraqi specifications and the World Health Organization and the US Environmental Agency to protect drinking water.

| Trace elements | Range (ppb) | Mean (ppb) | IQS, 2009 (ppb) | WHO, 2011 (ppb) |
|-----------------------|----------------------|-------------------|------------------------|------------------------|
| As | 0.7 - 3.8 | 1.47 | 10 | 10 |
| Ba | 15.08 - 66.18 | 35.98 | 700 | 700 |
| Br | 98 – 589 | 209.46 | ----- | 10 |
| CO | 0.02-0.2 | 0.0638 | ----- | ----- |
| Cr | 7.7-47.8 | 21.92 | 50 | 50 |
| Sr | 899.13-9197.6 | 4912.4 | ---- | ----- |
| Zn | 11 -1821.4 | 313.75 | 3000 | 3000 |
| Si | 6585 - 12515 | 10022.2 | ----- | ----- |
| U | 2.23-9.54- | 5.81076 | ----- | 30 |
| V | 8.3-19.1 | 11.261 | ----- | ----- |
| S | 126-352 | 229.9 | ----- | ----- |
| Fe | 21-2131 | 195.125 | 300 | 3000> |
| Mn | 0.38-137.51 | 14.9 | 100 | 400 |
| Mo | 2.5 - 12.7 | 6.34 | ---- | 70 |
| Ni | 5 – 13 | 8.2 | 20 | 70 |
| Pb | 25-50 | 39 | 10 | 10 |