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THE INFLUENCE OF WASTE DISPOSAL SITE ON THE WATER AND SOIL QUALITY IN HALABJA PROVINCE, KURDISTAN, IRAQ

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ABSTRACT:

Solid waste disposal could be a major environmental problem in in Kurdistan region of Iraq because it is not managed properly. The main purpose of this study was to assess the influence of long term solid waste disposal on water and soil physicochemical properties. Soil and water samples were collected in and around the solid waste disposal area. The samples were analyzed for physicochemical characteristics and potentially toxic elements using ICPMS. The results revealed that some water parameters analysed well below WHO and EU standards for drinking water. Therefore, the surface and ground water samples in this study are good for drinking purposes. However, the application of water quality index (WQI) suggests that the ground and surface water around the open dumpsite are marked as good and poor water in quality respectively. High concentration of Ca in all soil samples is expected because the regional geology is calcareous. The concentrations of PTEs were found in order of Mn> Fe> Ni> Zn> Cr> Cu> Pb> Se> Cd. Although relatively high concentrations of Ni and Cr were found at all sampling points, mean concentrations of trace elements in the soil samples in the studied area were all below the soil guideline values (SGV). Enrichment factors (EFs), calculated using typical carbonate bedrock geologies, confirmed that there was typically significant enrichment in trace elements above expected background concentrations. Whereas concentrations of toxic elements were within the 'safe' limits in the studied area were solid disposing of wastes in the outskirt of the city could lead to PTE accumulation in surrounding water soils.

KEYWORDS: Solid Waste Disposal, Potentially Toxic Elements, Water Quality Index, Enrichment Factor.

1. INTRODUCTIONS

The management of solid waste could be accounted as main sources of environmental contamination in developing countries. The majority of wastes are produced in urban areas. It's believed that, more than half of the wastes in developing would not be utterly treated (Pasquini and countries Alexander, 2004).. Domestic solid waste could be consider a source of organic and inorganic contamination ,for instance, domestic chemical contaminants, cans of foods, electrical compartments and batteries, ceramics, paints, components of automobiles plastics and oil, , inks, wastes of construction and hospital (Nabulo et al., 2012). As a result of indiscriminate disposal and dumping of solid waste may likely lead to spreading diseases, accumulate pollutants in soils and water consequently cause changes in water and soil physicochemical properties and distort interaction among biological, chemical and physical soil functions. (!!! INVALID CITATION !!!) Former research has reported that crops and vegetables grown in or around waste disposal area contain higher concentrations of PTEs than those grown in clean soil (!!! INVALID CITATION !!!).

Within some limits, the organic portion of municipal waste, for example, kitchen wastes from raw materials obtained in the consumption and preparation of food (wastes of food, nasty fruit, leafy vegetables, crop leftover, animal wastes (bones and excreta) (Asomani-Boateng and Murray, 1999, Adjia et al., 2008), these kind of wastes can improve soil fertility in urban farming and develop the physical property of soil (Anikwe and Nwobodo, 2002). The creation of compost from organic portion of domestic waste and its utilize in UPA may have a significant role in soil organic matter improvement (Gigliotti et al., 1996), and maintain physical and biochemical criteria of impoverish soil. Moreover, it is a unique substitute to incineration and dumping ,reducing CO_2 and atmospheric contaminant emissions (Baldantoni et al., 2010).

On the other hand, high concentration of different water and soil contaminants in composting materials and technique has been reported (!!! INVALID CITATION !!!), may lead to soil and water. The different contaminants might be accumulated in the soil and may cause environmental risks as they could be absorbed by plants and passing through food webs or leach through the soil thus contaminate ground water (!!! INVALID CITATION !!!), as well as, colloidal and dissolved organic matter in compost structure may lead to bioavailability and lability of potentially toxic elements (!!! INVALID CITATION !!!).

In Kurdistan region of Iraq, particularly in the present study areas (Halabja province), solid wastes including domestic, hospital and industrial wastes all together are being disposed or some time partially dumped in somewhere close to the city, where people are practicing many kinds of agriculture especially crop production. Only in Halabja city Approximately 1 kg per capita per day of solid waste is being produced and about 100 tons of wastes are transferred by the municipal vehicles (dumper, tractors, and trucks) into solid waste disposal area. The pile of waste in the waste disposal area is set on fire either by waste scavenger or by self-incinerating consequently different of gas pollutants may release into the air also during the rainy seasons (winter and spring) the leachate from the disposal area flows in the river and/or filtrates in to

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ground water which farmers totally depending on for agriculture activities. The main aims of this study were to assess the influence of waste disposal on the water and soil quality in the area near by the wastes disposal.

2. MATERIAL AND METHODS

2.1 Description of the area

The waste disposal site in Halabja is situated in the north west of Halabja city, longitude 45°56'57.65"E and latitude 35°12'28.08"N. The area is used by Halabja city council as a disposal and dumping place for municipal, hospital and industrial wastes. Land around the area is used to grow food crops mainly for commercial purposes, any kinds of recyclable and hazardous waste is also disposed including plastic, glass, metal waste and batteries. About three artesian well water and 4 surface (river) water samples were taken and 7 soil samples were collected for 6 months in and around study area (Fig1)

2.2 Sample preparation

Soil samples were taken from May to December 2014, using a stainless and clean steel trowel and put in polyethylene disposable bags for transport to a laboratory at the college of applied science in Halabja. The samples were dried in trays made out of aluminum. After the samples were completely dried, they slowly disaggregated by mortar and pestle then sieved to perform a <2 mm soil fraction. Approximately 25g of each sample were put into polyethylene tubes and transported to, UK. A portion of each sample was ground finely using an agate ball mill (Retsch, Model PM400), and then stored in polyethylene bags for for elemental analysis.



Figure. 1 Map of Halabja Province showing selected areas in which sampling points are demonstrated. Red markers denote to soil samples and blue marks denote to water samples

Water samples were taken from May to December 2014, with a polythene bucket, all sample containers and laboratory glasses used in analytical processes were washed with distilled water and soaked with 10% HCl solution followed by twice rinsing with distilled water, samples were transferred in a cool box when the temperature was more than 25 0C and transferred to the laboratory as soon as possible. Water samples were transported to the laboratories of Directorate of Health Prevention in Sulaimani city for analysis of some parameters. The samples were acidified with 1:1HNO3/D.W for heavy metals detection to minimize the precipitation and adsorption to the container wall were acidified with concentration HNO3 to bring pH < 2, and stored in refrigerators for later determination.

2.3 Physicochemical characteristics of water and soil

Physicochemical parameters of water such as pH, EC, TDS, alkalinity DO, BODs, total, calcium and magnesium hardness, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , $NO2^-$, $NO3^-$ and $SO4^{2-}$ were analyzed based on the standard techniques showed in APHA, (1985). As well as, physico-chemical parameters: pH, electrical conductivity of soil were measured based on the standard reported by

2.3.1 Multi-elemental analysis: Analysis of multi element was performed by ICP-MS (Model X-SeriesII , Thermo-Fisher Scientific, Bremen, GermanyExternal multi-element

(Claritas-PPT grade calibration standards CLMS-2. Certiprep/Fisher) included Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Rb, Se, Sr, U,V and Zn, all in the suitable range of 0-100 μ g L⁻¹. Processing of Sample was done by a software called Plasma lab (version 2.5.4; Thermo-Fisher Scientific) set to manage internal crosscalibration and separate calibration blocks where necessary. For each digestion group of data were corrected through digestions of two blank and quality assessing control with the samples of a reference material which are (Standard Reference Material (SRM) 2711, Montana Soil) from the National Institute of Standards and Technology (NIST). All elemental concentrations were converted to $mg kg^{-1} dw$ (equation 1).

$$C_{soil} = \frac{(C_{soil} * C_{blank}) \times Vol}{W_{soil}} \qquad | \qquad Eq. (1)$$

where C_{soil} is the elemental concentration (mg kg⁻¹) in the soil; C_{sol} and C_{blank} are the concentrations (μ g L⁻¹) in the soil and blank digests, corrected for dilution, Vol is the digest volume (50 mL) and W_{soil} is the mass of soil digested (c. 200 mg).

2.4 Water quality Index

Estimating water quality index is to make the information very easy and understandable for public. And act as indicator for the measuring water quality (Khwakaram et al., 2012). In the present study, Water Quality Index (WQI) was estimated by using the Weighted Arithmetic Index method as mentioned by Cude (2001). In this approach, various water quality portions are multiplied by a weighting factor and are then aggregated by arithmetic average. The stages for Water quality index (WQI) are: The quality rating scale for each parameter qi was calculated by using this equation:

 Table 1. Maximum, minimum, mean values, and standard deviation of the variables determined in the ground water samples

| Variables | Min-Max | Mean values | Std. |
|-----------------------------|-----------|-------------|------|
| | | | Dev. |
| Temperature (°c) | 17.4-19.5 | 18.2 | 0.9 |
| pH | 7.5-7.9 | 7.8 | 0.2 |
| Conductivity µs/cm | 357.3- | 377.9 | 19.5 |
| | 406.7 | | |
| Dissolved Oxygen | 7.2-7.8 | 7.5 | 0.3 |
| mg.l ⁻¹ | | | |
| Biological oxygen | 4.1-4.4 | 4.2 | 0.1 |
| demand (BOD) mg.1-1 | | | |
| Total hardness | 265.3- | 286.3 | 16.9 |
| mgCaCO3.1 ⁻¹ | 305.3 | | |
| Calcium Hardness | 55.3-74.3 | 64.9 | 7.1 |
| mgCaCO3.1 ⁻¹ | | | |
| Magnesium | 42.3-57.7 | 49.3 | 6.2 |
| Alkalinity mg.1-1 | 194.3- | 224.1 | 36.1 |
| | 271.3 | | |
| Chloride mg.1 ⁻¹ | 55.7-63.7 | 60.9 | 3.5 |
| Nitrate mg.1-1 | 9.3-16.1 | 12.6 | 2.5 |

 $qi = (Ci / Si) \times 100.$ Eq (2)

Where; qi; A quality rating scale for each parameter is assigned, Ci; dividing each parameters concentration in the water sample through, Si: parameters respective standard, Wi; the Relative (unit) weight. For the corresponding parameter using the following equations;

 $Wi = 1/Si \qquad Eq (3)$

Where, Wi: Relative (unit) weight for th parameter, Si: Standard permissible value for nth parameter, I; Proportionality constant. Finally, the overall WQI was estimated by combining the rating of quality with the unit weight linearly using the below equation:

Eq (4)

2.5 Statistical analysis

Statistical analysis of data was carried out using SPSS v. 17 statistical packages and Minitab v.16 was used for Pearson correlation, principal component and cluster analysis. These methods were used to analyse the multivariate correlation among soil properties and major and trace element concentrations.

3. RESULT AND DISCUSSION

Physico-chemical properties of ground and surface water are listed in Table 1 and 2 with minimum, maximum, mean and SD values for six month waster sampling. The guideline value of pH in surface water ranged from 6.0 to .5 while ground water from 6.5 to 8.5 (Patel et al., 2004). Therefore, pH of all water samples at the current studied areas (surface and ground) is within safe limits for drinking purposes. It is not uncommon in the Iraqi Kurdistan region for the pH value of water to be characterized by a shift toward the alkaline side of neutrality (above 7) because of the geological formation of the area which is calcareous (Nabi, 2005). The mean value of EC of ground water (478.3 μ S/cm) was significantly higher than the mean value for surface water (377.9 μ S/cm) at all sampling sites.

The dissolved oxygen (DO) concentration depends on the physical, chemical, and biochemical activities in water body

and its measurement is a good indication of water quality. (WHO/EU, 1983). Dissolved oxygen concentration in well water samples ranged from ($5.8-7.3 \text{ mg.l}^{-1}$) with mean for the study period during the entire sampling time. While, dissolved oxygen in the surface water samples ranged from $7.2-7.8 \text{ mg.l}^{-1}$ with mean of 7.5. The results disagreed with the results performed by Rashid (2010)

| Table 2. Maximum, minimum, mean values, and standard deviation |
|--|
| of the physico-chemical parameters determined in the surface water |
| 1 |

| Variables | Min-Max | Mean values | Std. Dev. |
|--|------------|-------------|-----------|
| Temperature (°c) | 18.1-27 | 21.5 | 3.1 |
| pH | 6.5-7.4 | 7.03 | 0.31 |
| Conductivity µs/cm | 363-662.3 | 478.3 | 115.2 |
| Dissolved Oxygen mg.l ⁻¹ | 5.8-7.3 | 6.4 | 0.42 |
| Biological oxygen demand (BOD) mg.l ⁻¹ | 2.8-3.8 | 3.2 | 0.22 |
| Total hardness mgCaCO3.1 ⁻¹ | 250-413.7 | 301.5 | 67 |
| Calcium Hardness mgCaCO3.1 ⁻¹ | 61.7-147.3 | 94.6 | 25 |
| Magnesium | 37.3-77 | 49.6 | 10.6 |
| Alkalinity mg.1-1 | 175-246 | 212.8 | 22.2 |
| Chloride mg.1-1 | 70-195 | 97.5 | 36.9 |
| Nitrate mg.1-1 | 9.3-17 | 13.3 | 2.1 |

The effect of a waste discharge on water resources is largely determined by oxygen balance of the system. Also, seasonal oscillations in dissolved oxygen might be attributed to several other reasons; water temperature, dissolved salts, partial pressure of the gas, wind, as well as inputs of organic matter and process of organic matter degradation (Nasir, 2007). Oxygen depletion during August in W3 is coincident with high water temperature as well as high microorganism's densities that created anaerobic condition as a result of organic matter decomposition(Sawyer et al., 1978). However, the author stated that the dissolved oxygen concentration in polluted water was much less than in pure water. DO levels can provide information on the concentration of oxygen demanding pollutants that may be entering surface water via point and nonpoint sources. Oxygen is consumed by microorganisms as they degrade organic matter in water; as a result the DO concentration decreases(Elbag, 2006).

Biological oxygen demand (BOD) is defined as the amount of oxygen required by decomposers while stabilizing decomposable organic matter under aerobic condition. Biodegradable organic material creates biological oxygen demand (BOD₅) which can cause low dissolved oxygen, which in turn creates taste and odor problems in well water, and cause leaching of metals from soil and rock into ground water and surface waters (Eaton et al., 2005).

BOD in ground water samples ranged from $2.8 - 3.8 \text{ mg.}\text{l}^{-1}$ with mean $3.2 \text{ mg.}\text{l}^{-1}$, whereassurface water value ranged from $4.1 - 4.4 \text{ mg.}\text{l}^{-1}$ with mean of $4.2 \text{ mg.}\text{l}^{-1}$. This concentration was higher than those obtained by Rashid (2010), this may refer to the difference in water resources have been used for the studies. High level of BOD in this study may have related to the amount of rainfall that washes down all pollutants from water disposal areas and put in to surface water. It may also indicate the presence of high amount of microorganisms which could be attributed to the microbial demand for oxygen, because (BOD₅) is the amount of dissolved oxygen needed by certain species of bacteria while stabilizing degradable organic matter (Sawyer et al., 1978).

During the hot seasons, the amount of BOD₅ increased, which may be due to the increasing activity of microorganisms that consume DO in oxidation processes .Hynes (1960) According to the permissible standards, wells water can be classified as fairly clean but surface water classified as doubtful water quality. In general, leachates from landfills change the biological properties of the aquatic systems because of high input of organic matter; the growth of bacteria is stimulated. This excess of bacteria causes a rise in the biological oxygen demand (BOD) which may end up in a depletion of oxygen in the water system (Schwarzbauer et al., 2002).

Total hardness is a measure of the concentration of calcium & Magnesium and /or iron in water and its usually expressed as the equivalent to CaCO₃ concentration (Meybeck et al., 1996). In the present study, the value of ground water total hardness ranged between 250 - 413.7 mg CaCO₃.l⁻¹ with an average 301.5 mg CaCO₃.l⁻¹ while the concentration for surface water ranged from 265.3-305.3 with mean 286.3 mg CaCO₃.l⁻¹. These results showed different values of total hardness which may be due to the source and type of water resources, the geological background and soil properties of the studied area. The results of all water sample relating to the total hardness as CaCO₃ are within the permissible limits recommended by (WHO/EU, 1983) 500 mg.l-1. The results of the present investigation is closely related to the observations obtained by Rashid (2010).

Cations in natural waters are generally dominated by calcium followed by magnesium, sodium and potassium according to their decreasing order of concentration (Galat et al., 1981). Magnesium is usually less abundant in waters bodies than calcium, which is normal as magnesium is present in the earth's crus much more than the calcium concentration. Calcium hardness was more than magnesium hardness in this study where well water Calcium hardness ranged from 61.7 - 147.3 mg CaCO₃.l⁻¹ with an average 94.6 mg CaCO₃.l⁻¹, while magnesium hardness ranged between 37.3 – 77.0 mg CaCO₃.l⁻¹ with an average 49.6 mg CaCO₃.l⁻¹. On the other hand, the value of surface water Calcium hardness ranged from 55.3 – 74.3 mg CaCO₃.l⁻¹) with mean 64.9 mg CaCO₃.l⁻¹, while magnesium hardness ranged from 42.3 - 57.7 mg CaCO₃.l⁻¹ with mean 49.3 mg CaCO₃.l⁻¹.

According to WHO standards for drinking purpose, the maximum desirable concentration level of calcium is 75 mg CaCO₃.l⁻¹ and the permissible concentration level is 200 mg CaCO₃.l⁻¹ while the high desirable level of magnesium concentration is 50 mg.l⁻¹ and the permissible level of Mg concentration is 150 mg.l⁻¹. The concentration of Ca and Mg hardness for all wells & surface water in the studied areas lie within this limit and is considered safe for drinking according to FAO/WHO (2001)

The dominance of calcium ion on magnesium ion recorded in all stations during the present study is in agreement with the result obtained by many researchers including (Mustafa and Ahmad, 2008, Raman and Narayanan, 2008). The high concentration of Ca than Mg in this investigation may have attributed to the geological formation of the study area which is composed mainly of limestone and that solubility of calcite rocks which is abundant in the area, is more rapidly than dolomite(Ali, 2002) and may also be possibly due to the degree of the ability of cations to precipitate as carbonate compounds (Golterman and De Oude, 1991), or various bicarbonate and carbonate compounds, originating from dissolution of sedimentary rocks. On the other hand, the excess in calcium concentration may result from the mixing of water and leachate effluents from the waste disposal sites.

Total alkalinity is generally associated with the presence of carbonates, bicarbonates and hydroxides and some less significant constituents. High alkalinity in water is undesirable because it causes excessive hardness and can result in high concentrations of salts. Acceptable limits have been established to alleviate corrosive or encrusting properties and eliminate human health problems such as gastrointestinal (stomach) irritation (Al Aswad et al., 1978, Carr and Neary, 2008). In this study the mean value of alkalinity was 224.1 mg.l⁻¹ for surface water, while it was 212.8 mg.l⁻¹ for well water samples which

can mainly be contributed to OH, CO3, HCO3 ions. The same results were indicated by many other researcher (!!! INVALID CITATION !!!).

| Table 3. Concentrations of trace elements ($\mu g L^{-1}$) of ground water |
|--|
| samples with Minimum, Maximum, mean, SD and FAO/WHO guide |
| 1' 1 |

| | 1 | he values | | |
|----------|-------------|-------------|----------|------|
| Elements | Min-Max | Mean values | Std. Dev | GV |
| Na | 2460-15480 | 7256.67 | 7154.48 | |
| Mg | 10130-15210 | 12176.67 | 2679.88 | |
| K | 890-1560 | 1116.67 | 383.97 | |
| Ca | 59660-72900 | 65986.67 | 6639.47 | |
| Al | 11.15-28.34 | 19.85 | 8.60 | |
| V | 3.74-7.99 | 5.86 | 2.13 | |
| Cr | 2.35-3.92 | 2.92 | 0.87 | 50 |
| Mn | 13.23-20.38 | 11.50 | 9.85 | 200 |
| Fe | 10.59-31.5 | 22.90 | 10.94 | 5000 |
| Co | 0.03-0.25 | 0.14 | 0.11 | 50 |
| Ni | 0.85-4.16 | 2.53 | 1.66 | 200 |
| Cu | 0.30-1.27 | 0.80 | 0.47 | 200 |
| Zn | 15.08-64.96 | 39.03 | 25.00 | 2000 |
| As | 0.39-0.85 | 0.58 | 0.24 | 10 |
| Se | 0.58-1.08 | 0.86 | 0.25 | |
| Sr | 481-1398 | 802.33 | 516.40 | |
| Mo | 2.34-14.83 | 9.34 | 6.38 | |
| Cd | 0.01-0.04 | 0.02 | 0.02 | 10 |
| Cs | 0-0.01 | 0.003 | 0.006 | |
| Ba | 57.13-124.6 | 89.34 | 33.84 | |
| Pb | 0.23-0.076 | 0.13 | 0.09 | 5000 |
| U | 0.98-1.02 | 1.27 | 0.47 | |

The concentration of chloride ion in the ground and surface water adjacent to solid waste dumping sites ranged between 70 mg.l⁻¹ to 195 mg.l⁻¹ with mean value of 97.5 mg.l⁻¹ and 55.7 mg.l⁻¹ to 63.7 mg.l⁻¹ with average 60.9 mgL⁻¹ respectively. According to (WHO, 2011) the maximum desirable value is 250 mg.l⁻¹ thus, all investigated wells and surface water contain desirable chloride concentrations .

These results came in agreement with (Mustafa and Ahmad, 2008, Muhammad et al., 2011), while the results obtained by this study were lower than those obtained by Mustafa et al. (2006). The author reported high chloride concentration in groundwater of AL-Dora in Baghdad city this may be due to domestic rather than agricultural. High chloride levels in groundwater can contribute significantly to infiltration by sewage and leachates (Bocanegra et al., 2001).

Nitrate considered as the oxidizable form of nitrogen complexes; it is usually found in water bodies because nitrate is the end product of the aerobic decomposition of nitrogenous organic matter (Meybeck et al., 1996). There are many sources of nitrates including, manure, sewage, deposit form of nitrate wastes of animal, compost, residues of plants, nitrogen fixation ,fertilized nitrogen (Organization, 2004). Natural water with less pollution contain only low amount of nitrate , its concentration in the water bodies (ground and surface) is normally minute but can elevated because of leaching or runoff from agricultural activities or manmade contamination consequently lead to the oxidation of ammonia and similar sources (WHO/FAO, 2007).

Well water and surface water nitrate concentration ranged from $9.3 - 17 \text{mg.I}^{-1}$ with mean 13.3 mg.I^{-1} and $9.3 - 16.1 \text{ mg.I}^{-1}$ with mean 12.6 mg.I^{-1} . The maximum value was recorded at W1, the reason of increase in nitrate may have related to the effect of the disposal site. These findings were higher than those reported by (Ologundudu, 2009, Nwankwoala, 2013) but lower than those reported by Rashid (2010)

It is noted that high nitrate concentration was more in W1 which is close to the landfill site. Manure which is high in nitrate is used as a fertilizer hence large amounts of nitrates find their way into the ground water. While, the source of nitrate pollution in surface waters may be related to dumping leachate disposal and to some extent agricultural activities (Rashid, 2010). According to (WHO/EU, 1983)the guideline values for nitrate is recommended to be 50 mg at NO₃-N.I⁻¹ accordingly

all wells and surface water lied within the recommended level of nitrate-nitrogen for drinking purposes. Nitrate in groundwater originates primarily from fertilizers, septic systems, and manure storage or spreading operations. Normally the contaminants made by the waste disposal during degrading the decomposable portion of the waste enter into the surface and ground water then influencing the quality and ecological health of the water bodies (Carpenter et al., 1998)

3.1. Trace metal concentrations

The concentration (μ g/l) of trace metals in ground water was highest for Sr followed by Mn, Ba, Fe, Zn, Al, Ni, V, Mo, Cr, As, Cu, Co, Se, U, Pb, Cd and Cs, respectively (Table 3). Also the highest metal concentration in surface water was Sr and the order observed for other metals was Ba >Zn>Se> Al>Mn>Mo>V >Cr>Ni >As>Cu>U >Se >Pb >Co >Cd >Cs (Table 4). According to Pescod (1992)(1992), maximum permissible values of trace metals in water were Zn (2000 μ g L⁻¹), Cu (200 μ g L⁻¹), Fe (5000 μ g L⁻¹), Mn

 $(200 \ \mu g \ L^{-1})$, Ni $(200 \ mg \ \mu g \ L^{-1})$, Pb $(5000 \ \mu g \ L^{-1})$ and Cd $(10 \ \mu g \ L^{-1})$. In this investigation, although elevated concentrations of some metals have been found in ground water compared to surface water, the concentrations of the trace elements in these sources of water were within the standard limits.

Table 4. Concentrations of trace elements (μ g L⁻¹) of surface water samples with Minimum, Maximum, mean, SD and FAO/WHO guide line values.

| Elements | Min-Max | Mean values | Std. Dev | GV |
|----------|-------------|-------------|----------|------|
| Na | 4470-14970 | 9720 | 7424 | |
| Mg | 6010-13690 | 9850 | 5430 | |
| K | 930-950 | 930 | 28.2 | |
| Ca | 59420-6088 | 59420 | 2064 | |
| Al | 12.98-21.86 | 17.42 | 6.27 | |
| V | 1.38-8.8 | 5.09 | 5.24 | |
| Cr | 1.02-5.52 | 3.27 | 3.18 | 50 |
| Mn | 1.34-2.03 | 1.685 | 0.487 | 200 |
| Fe | 18.89-32.98 | 25.935 | 9.963 | 5000 |
| Co | 0.04-0.06 | 0.05 | 0.014 | 50 |
| Ni | 1.23-4.0 | 2.615 | 1.95 | 200 |
| Cu | 0.6-4.02 | 2.31 | 2.41 | 200 |
| Zn | 15.52-27.47 | 21.495 | 8.44 | 2000 |
| As | 0.4-5.87 | 3.135 | 3.86 | 10 |
| Se | 0.16-0.49 | 0.325 | 0.233 | |
| Sr | 234-1320 | 777 | 767 | |
| Mo | 2.37-2.82 | 2.595 | 0.318 | |
| Cd | 0.02-0.08 | 0.05 | 0.042 | 10 |
| Cs | 0.01-0.05 | 0.03 | 0.028 | |
| Ba | 32.16-50.26 | 41.21 | 12.7 | |
| Pb | 0.14-1.36 | 0.75 | 0.862 | 5000 |
| U | 0.34-1.6 | 0.97 | 0.890 | |

(2012)Lente et al. (2012) found almost the same trace metals concentrations in both ground water and surface water used for drinking purposes. The authors stated that, it is normal to find such levels of trace elements in well and surface water. Solid waste is being deposed relatively far from the disposal sites, consequently the contaminants emanated from the waste may have not reached the water sources. Additionally, there are no localized industrial activities in the areas; therefore most of the wastes come from domestic sources including hospitals and institutions. Related studies on water near to liquid and solid waste disposal in two cities of Kurdistan region have estimated similar trends (!!! INVALID CITATION !!!).

In general there was no obvious variation between these two water sources (ground and surface) at waste disposal sites in respect of Cr, Cu, Cd, and Pb. However, at the points near by the pile of waste high concentrations of elements (Cu, As and Cd) have been found in ground water compared to the surface water whereas, at the rest of the sampling points some metals like Co, Cu, Cd, Pb and Ni are significantly higher in ground water.

Possible correlations were observed between trace element concentrations in the waterthroughout the study, using scatter plots as shown in Fig.2. The statistical relationship between metals is related to their same common sources. For example, the strong positive correlation between Pb and Cd with Cu (R^2 =0.89 and (R^2 =0.85, respectively), and Ni with Co (R^2 =0.80) were related to their solid waste as a source of metal contaminationsources (Navarro et al., 2008). There was a strong correlation between K and Na (R^2 =0.87) which suggests that they may originate from similar sources (Bhuiyan et al., 2010).

3.2. Water Quality index (WQI):

Application of (WQI) in the present investigation was found useful in evaluating the water quality and to make accurate decision on the water quality. This approach considered as more systematic and offers a comparative assessment of the quality of waters at the sampling points. It is also useful for the consumers to understand the water quality besides of other fields in public health and water quality management. (Khwakaram et al., 2012.

The mean of WQI for ground and surface water were 90.23 and 102.5 respectively during the studied period (Table 5 and 6) hence, the water can be recognized as "good water" for ground water and "Poor water" for surface water according to water quality classification based on WQI Table 7.



Figure 2. Bivariate scatter plots for some trace elements in water samples showing high correlation values

| Table 5. Calculation of water quality index via ground water sample | | | | | | |
|---|--|---|--------------------------------------|---|--|--------------------------------------|
| Parameters | Unit | Actual measured value | WQ standard value (Si) | RelativeWQualityI(Wi)(Q | /eight Rating Qi) | Weighted Value (QiWi) |
| pН | | 7.03 | 6.5 - 8.5 | 0.133 | 93.7 | 12.46 |
| EC | μs.cm ⁻¹ | 478.3 | 1000 | 0.001 | 47.83 | 0.048 |
| DO Total hardness Calcium hardness Magnesium Alkalinity | mg.l ⁻¹ mg.l ⁻¹ mg.l ⁻¹ mg.l ⁻¹ | 6.4 301.5 94.6 49.6 212.8 | 5 100 100 30 200 | 0.2 0.01 0.01 0.033 0.005 | 128 301.5 94.6 165.3 106.4 | 25.6 3.02 0.95 5.45 0.53 |
| Sodium Potassium Chloride Nitrate | mg.l ⁻¹ mg.l ⁻¹ mg.l ⁻¹ mg.l ⁻¹ | 5.8 0.9 97.5 13.3 $\sum Wi = 0$ | 20 10 250 50 0.566 ∑QiWi | 0.05 0.1 0.004 0.02 i= 51.098 | 29 9 39 26.6 | 1.45 0.9 0.16 0.53 |
| Water quality index (W | QI) = 90.23 | - | | | | |

| | Table 6. | Calculation of water q | uality index via surface | water samples | | |
|------------------|---------------------|------------------------|------------------------------|-----------------|------------------|--------------|
| Parameters | Unit | Actual measured | WQ standard value | Relative | Weight | Weighted |
| | | value | (Si) | Quality (Wi) | Rating (Qi) | Value (QiWi) |
| pH | | 7.8 | 6.5 - 8.5 | 0.133 | 104 | 13.83 |
| EC | µs.cm ⁻¹ | 377.9 | 1000 | 0.001 | 37.79 | 0.038 |
| DO | mg.l ⁻¹ | 7.5 | 5 | 0.2 | 150 | 30 |
| Total hardness | mg.l ⁻¹ | 286.3 | 100 | 0.01 | 286.3 | 2.86 |
| Calcium hardness | mg.l ⁻¹ | 64.9 | 100 | 0.01 | 64.9 | 0.65 |
| Magnesium | mg.l ⁻¹ | 49.3 | 30 | 0.033 | 164.3 | 5.42 |
| Alkalinity | mg.l ⁻¹ | 235.1 | 200 | 0.005 | 117.5 | 0.59 |
| Sodium | mg.l ⁻¹ | 7.8 | 20 | 0.05 | 39 | 1.95 |
| Potassium | mg.l ⁻¹ | 2.1 | 10 | 0.1 | 21 | 2.1 |
| Chloride | mg.l ⁻¹ | 60.9 | 250 | 0.004 | 24.36 | 0.097 |
| Nitrate | mg.l ⁻¹ | 12.6 | 50 | 0.02 | 25.2 | 0.5 |
| | | $\sum Wi = 0.560$ | $5 \qquad \sum QiWi = 58.04$ | | | |

Water quality index (WQI) = 102.5

Table 7. Water quality classification based on WQI value(Ramakrishnaiah et al., 2009)

| value(Ramakrisinialan et al., 2007) | | | | |
|-------------------------------------|----------------------------|--|--|--|
| Description | Water Quality Index levels | | | |
| Excellent | <50 | | | |
| Good water | 50-100 | | | |
| Poor water | 100-200 | | | |
| Very poor (bad) water | 200-300 | | | |
| Unsuitable (unfit) for drinking | >300 | | | |

3.3. Variation in soil pH and organic matter with sampled areas

Soil pH and organic matter are considered to be significant factors which control trace element mobility, accumulation and bioavailability. At high pH the lability and bioavailability of trace elements decrease due to precipitation of carbonate and hydroxides or organic complex formation, while their mobility increases when the pH decreases (Xu et al., 2010). The range of pH and organic matter (LOI %) values at all studied areas are given in Fig.3. The mean soil pH value ranged from 7.9 at S5to 8.3 at S2 ; there is no significant difference between sampled points because the soil in the study area (Halabja province) is alkaline and calcareous in nature and classified by silty loam, sandy and silty clay (Rashid, 2010). As well as, this alkalinity can be ascribed to the high content of carbonate gravel and CaCO₃. Rashid (1993) stated that the CaCO₃ percentage in the northern part of Iraq (Kurdistan region of Iraq) ranged from 3.8 to 65 percent. Additionally, most of the investigations indicated that, the soil pH increased after prolonged application of untreated waste water (Kunhikrishnan et al., 2012). Several studies stated that soil pH is not influenced by waste water irrigation (Gwenzy and Munodo, 2008) while,(Rattan et al., 2005) and (Xu et al., 2010) reported decreased pH of waste water irrigated soil.

LOI is an estimation of the percentage of organic carbon in soil. The organic carbon of the soil samples ranges from 6.6% at S4 to 11% at S2 with a mean of 9.2%. The highest value was in S2 because of the influence of municipal waste disposal on the soil properties. Anikwe (2002) recorded high organic matter in the dump site compare to the non-dump site. In addition, waste water application releases more organic matter to a soil than rain or clean water. Many studies conducted in long term sewage water irrigated soils showed high soil organic matter content in the topsoil (!!! INVALID CITATION !!!). On the basis of these results, the mobility and bioavailability of PTEs would be predicted to be low in the agricultural soils in the sampling areas.

The agricultural fields in those areas are exposed to heavy rain, in rainy seasons, and to periodic flooding by rivers following heavy rain, which may lead to variation in as concentrations around the year. The Se concentration in the soil mainly relies on the Se concentration in the bed materials and on the degree of weathering and leaching of the area in addition to anthropogenic activity (Bajaj et al., 2011). This result was in agreement with the findings of Roychowdhury (2002). There was not found to be any noticeable variation between Se concentrations at all sampling areas and the concentrations determined were similar to those found in agricultural soils (0.20–4.38 mg kg⁻¹) of other semi-arid regions (!!! INVALID CITATION !!!).

3.4. Trace metal/oid concentrations in agricultural soils

3.4.1 Metalloids: (As and Se): The mean concentrations of metalloids (mg /kg) in agricultural soils of the study areas Fig 4 ranged from 4.7 at Sulaymanyah sampling sites (S3) to 13.5 at each S7 and S1 sampling points for As and from 0.7 S4 rier sampling point to 1.7 at S7 sampling site for Se. Although wastewater irrigation is considered to be one of the significant sources of metalloids, the total metalloid concentrations were below the Soil Guideline value (Environment Agency, 2009). The As concentration at S1, S2 and S7 sampling points were significantly higher than the other soil sampling sites. This may be due to the application of pesticides and fertilizers as well as poultry manure

3.4.2 Hydrous oxide elements: (Fe and Mn): The mean concentrations and ranges were shown in Fig 5. The maximum concentration (mg/kg) for both Mn and Fe was recorded at the S1 (878.8 and 34986, respectively) while the minimum value was recorded at S3 sampling point (539.3 and 22021, respectively). The variation among Fe and Mn concentrations in the agricultural soil was attributed to irrigation of fields with untreated wastewater and other agronomic activities (Rahman et al., 2012).

3.4.3. Base elements: (Na, K, Mg and Ca): Major elements such as Na, K, Mg and Ca, were crucial elements for plant nutrition. They were occasionally found in plants in high concentrations because of their essentiality for agricultural plants, under optimal production conditions, would absorb a considerable amount of these metals. The results obtained during this study are given in Fig 6 where they are presented as means of total concentrations. In general, the order observed was Ca > Mg> K> Na. The concentrations were higher if compared to the other trace elements in the soil because of the essentiality of these elements for living organisms. In all studied sites calcium was the most abundant element and significantly higher than the other base elements with an average concentration of 99579 mg/kg among all investigated sites while the element with the lowest concentrations throughout all studied points was Na with an average concentration of 2778 mg.kg⁻¹. This result shows that soil with high calcium concentration has a very good association with soil mineral composition of primary and secondary minerals bearing calcium, for example, calcite, dolomite, plagioclas, smectite and mixed-layer-silicates (Jakovljeviã et al., 2003).



Figure 0. Mean and range of pH and LOI (%) values from all studied samples

Figure 1. Comparative box-plots of hydrous oxide metals (Fe and Mn) in the agricultural soils in the studied areas Figure 2. Mean concentrations of metalloids (As and Se) within the agricultural soil samples in the studied areas

3.4.5. Heavy metals (Cr, Ni, Cu, Zn, Mo, Cd and Pb)

The mean, range and SD values of 6 trace elements in agricultural soils are given in Table 8 arranged in the followed decreasing order: Zn> Cu> Pb>Cr>Ni> Cd. The results showed that the mean concentrations of toxic elements in the soil samples at the different study areas were all below the SGV. The lower concentrations of

these trace elements than the SGV in the study areas may be because they are continuously removed by the vegetation grown in the areas or due to leaching of the elements into deeper layers of soil (Singh et al., 2010). Moreover, the results of all elements in irrigation water were below FAO/WHO guideline value for irrigation water (FAO/WHO, 2001) which also supports these concentrations of metals in soil samples in the areas.

Table 8. Concentrations of toxic elements soil samples with



| Minimum, Maximum, mean, SD and guide line values | | | | | | |
|--|--------|--------|---------|-------|---------|--|
| Flomonto | Min- | Mean | Std. | SGVa | | |
| Liements | Max | values | Dev | 50 va | EU/WHOc | |
| C. | 72.66- | 124 | 124 264 | | | |
| CI | 152.3 | 134 | 50.4 | | | |
| NI: | 64.13- | 74.0 | 11.2 | | | |
| INI | 136.3 | /4.9 | 11.2 | | | |
| Cu | 20.79- | 262 | 155 | 250 | 50.0 | |
| Cu | 441 | 205 | 155 | 230 | 30.0 | |
| Zn | 67.64- | 772 | 102 | 50b | 100 | |
| ZII | 939 | 115 | 192 | 50 | 100 | |
| Cł | 0.38- | 4.10 | 1 66 | | | |
| Cu | 6.630 | 4.19 | 1.00 | | | |
| DL | 8.02- | 161.2 | 174 | | | |
| FU | 171.03 | 101.5 | 17.4 | | | |

^aSoil Guideline Values (SGV) for toxic metals (environment Agency, 2009a). ^bCu and Zn

4. CONCLUSION

Open dump area is considered a major environmental problem and may pose a serious threat to their surrounding environmental compartments including water and soil. Pollutants discharged from the waste disposal leachate which responsible for alterations of water and soil physico-chemical properties. The results showed that the waste disposal has significant adverse influence on the water quality, although the mean values of many parameters analyzed fell below WHO and EU standards for drinking water. Therefore, the application of WQI suggests that the groundwater around the open dumpsite is good water in quality, while surface water is poor water in quality because the open water is exposed to flow



waste leachate in. It can be concluded from this literature review and preliminary field study that the concentrations of all trace elements in wastewater irrigated soils are within the limits set by the Environment Agency but relatively high concentrations of Ni and Cr have been recorded which are very close to soil guideline value. Many studies indicated that the long-term influence of waste disposal sites may lead to the accumulation of chemicals which farmers and consumers may be exposed. While the concentrations of toxic metals do not surpass the permissible limits in areas studied, care should be taken particularly when the surrounding waste disposal area are used for agriculture purposes.

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