Assessment of Ground Water Pollution by Heavy Metals and Anions in Kwashe Industrial Area, Duhok City, Kurdistan Region. Iraq

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Abstract. Kwashe industrial area in Summel district, Duhok city, Kurdistan region-Iraq is relatively new and considered the only industrial area in Duhok city which include various factories such as petroleum refineries, dying, tanning, cement, recycling of steel in addition to large municipal waste separating factory that produce huge amount of wastes in huge landfill with high leachate. Therefore ten artesian wells were chosen nearby and downward industrial area to study the impacts of industrial effluents and landfill leachate in contaminations of these wells. The results showed. The sulfate content is under risk limit of WHO (3-150 µg/L) in ground water, but there is evidence that a little contamination plume is created in Girresh 28.63 ± 1.25 mg/L location. The Cl as typical recommended by WHO in ground water is 1-70 mg/L and are low in 5 artesian wells upper industrial area and magnified in the rest 5 artesian wells downward industrial area and high levels recorded in Girrash 30.33 ± 1.53 mg/L. WHO standard of NO₃ in ground water is 2-20 mg/L, the locations Kwashe 3, 4, 5 is better site of NO₃ in upper industrial area ranging between 5.13 ± 0.15 to 5.50 ± 0.20 and the third wells are save for drinking according WHO standards which must be under 10 mg/L are Kwashe 1, 2 and Sarshour ranging between 9.67 ± 0.1 and 9.70 ± 0.20 mg/L. The rest four wells Girresh, Marina, Moqebel, and Sarshour located down ward industrial effluents and landfill leachate are significantly affected toward increasing to reach hazardous levels in three location Sarshour 19.70 ± 1.45 mg/L, Marina location 22.67 ± 0.85 mg/L and the center of toxin plume recorded in Girrish 55.33 ± 0.25 mg/L which is not save as drinking water for adults and cattle babies according WHO standards. The typical soil properties like high pH values 7.9, huge amount of active/total CaCO₃ % 62.62 and high clay content 381.68 g/kg, makes the condition optimum for heavy metal precipitation and rendered it inactive in sorption site of soil colloidal system and prevent it to reach ground water table. However the little concentration of heavy metal are varied from location to another to give an index that the pollution is sever and create a toxin plume downward locations but not exceeded typical standards of WHO for drinking water.

Keyword: groundwater. Pollution. Industrial area. anions. heavy metal.

1. Introduction

Groundwater is essential part of fresh water used by humanity for drinking and irrigation nowadays, especially in arid and semi arid regions like Kurdistan region-Iraq where other sources of fresh water like springs and streams are depleted in most cases. So the awareness and attentions are paid all over the world to prevent ground water pollution by various contaminants like sewage sludge and industrial effluents (WWAP 2006). The industrial area of Kwashe in Sumail district, Duhok City, Iraqi Kurdistan region is constructed in about 2006 but it release a huge amount of non treated petrol effluents that contain hundreds of petrol derivatives, in addition to other effluents from tanning,
dying, and cement factories and large landfills of Kawashe waste recycling factories that release additional large amount of hazardous untreated leachate in the same area. The major use of water in this industrial area is as a solvent and as a component part of the industrial products. Discharged water from industrial areas are much greater than the amount consumed actually (WWAP, 2006). In regions where surface water resources are depleted or scarce like in Asia, groundwater is used to meet industrial demand like Kwashe industrial area in Kurdistan region where more than 10 artesian wells were used to meet industrial demands.

Groundwater usually contains heavy metals in minor concentrations. The major contamination sources of heavy metals in Kurdistan region-Iraq are fossil fuels industry, agricultural wastes, urban and industrial effluents, sewage sludge, and fertilizers. The tendency of heavy metals to bioaccumulate in the food chain is the most dangerous character of them; therefore they have high toxicity to human being even at low concentrations (Shashikanth et al. 2008). Fortunately heavy metals precipitated in groundwater in normal pH conditions (6.5 to 8.5) and become insoluble; therefore high concentrations of heavy metals in aquifers will not make a serious problem because it was immobile in most aquifers (Tiller 1989). Heavy metal contamination have greater risk in shallow, acidic ground water (W. H. O, 2008). So the aims of this paper are to assess the contamination of ground water caused by industrial effluents and landfill leachate especially heavy metals and hazardous anions like nitrate and sulfate.

2. Material and Methods:

2.1. Site description
Kwashe industrial area locate at about 20 km west of Duhok Governorate, Kurdistan region-Iraq, at national grid reference (36°59'04.2"N 42°47'50.8"E)

![Figure 1](image1.png)

**Figure 1.** The location of Kwashe industrial area and sites of water sampling from 10 artesian wells.

It has a flat physiographic area with an altitude of (555 m) above sea level. The area has a Mediterranean type climate with mean annual precipitation of (539mm) and mean annual temperature of (19.2 °C). The soil of the area is typified as silty clay loam with low content of organic matter (nearly 1.2%). The bedrock underlying the soil in this area is calcareous (Limestone) type and most important chemical and physical properties of soil are shown in table1.
2.2. Chemical Analysis
(10) Samples from ten wells of several sites where S1 to S5 inside the Kwashe industrial area and S6 Girrash village, S7 Marina village, S8 Sarshour village, S9 Moqeble village and S10 Tobzawa village are located the down ward of industrial area in different distance in south direction as shown in figure 1. Water and soil samples were taken and saved in colored bottle. Water samples were collected in January 2017 for chemical analysis. The determination of heavy metals lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), cobalt (Co), manganese (Mn), Aluminum (Al), Iron (Fe), Nickel (Ni), zinc (Zn) by standard analytic methods (APHA, 2005) and anions sulphate (SO\textsubscript{4}^2\textsuperscript{-}), chloride (Cl\textsuperscript{-}), (NO\textsubscript{3}^\textsuperscript{-}) were analyzed by spectrophotometer. The electrical conductivity of the saturation extract after equilibrium for 24 hours was measured with EC-meter Hesse (1972). The pH of the saturation extract was measured by pH-meter. The organic matter was measured with EC-meter Hesse (1972). The pH of the saturation extract was measured by pH-meter. The organic matter was determined by modified Wakley-Black method (Allison, 1965). Calcium carbonate was determined by acid neutralization method as outlined by Richards (1954). Cation exchange capacity (CEC) was also determined by using ammonium acetate according to Richards (1954). Soluble Ca\textsuperscript{2+} and Mg\textsuperscript{2+} were determined by complex metric titration with versenate (EDTA), the soluble Na\textsuperscript{+} and K\textsuperscript{+} were measured by flame photometer. Soluble HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} were determined using dilute HCl and soluble Cl\textsuperscript{-} by titration with AgNO\textsubscript{3} and K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} as indicator, as described by (Page et al., 1982).

| clay | PSD gm/kg | Text | Total% CaCO\textsubscript{3} | Activ% CaCO\textsubscript{3} | CaCO\textsubscript{3} (A/T)*100 | O.M% | pH |
|------|-----------|------|-----------------------------|-----------------------------|--------------------------------|------|-----|
| 381.68 | 418.85    | 199.47 | SICL | 24.75                       | 15.50                         | 62.62 | 1.18 | 7.90 |

| EC dS.m\textsuperscript{-1} | CEC cmol.kg\textsuperscript{-1} | SP% | Exchangeable Ca \textsuperscript{mg/100 g soil} | Ava.N \textsuperscript{mg.kg\textsuperscript{-1}} | Ava.Pmg. \textsuperscript{mg.kg\textsuperscript{-1}} | Ava.K \textsuperscript{mg.kg\textsuperscript{-1}} |
|-----------------------------|-----------------------------|-----|--------------------------------|-----------------------------|-----------------------------|-----------------------------|
| 0.55 | 29.12    | 44.42 | 22.53 | 56                          | 3.52                         | 25.3                        |

| Bulk density(gcm\textsuperscript{-3}) | Soluble Anions (mmole/L) | Soluble Cations (mmole/L) |
|-------------------------------------|--------------------------|---------------------------|
| 1.568 | Cl\textsuperscript{-} | 2.500  | Na\textsuperscript{+} | 0.179  |
| HCO\textsubscript{3}\textsuperscript{-} | 3.600  | K\textsuperscript{+} | 0.521  |
| CO\textsubscript{3}\textsuperscript{2-} | 0.600  | Ca\textsuperscript{2+} | 2.300  |
| SO\textsubscript{4}\textsuperscript{2-} | 0.400  | Mg\textsuperscript{2+} | 1.400  |

2.3. Statistical Analysis
Heavy metal concentrations in water of artesian wells were expressed as micrograms per liter (µg/L). One way ANOVA with general linear model (GLM) procedure was used to examine the significant changes (P ≤ 0.05) in the chemical properties and heavy metal among the studied area. Subsequently, Tukey's HSD (Honestly Significant Difference) test was used to indentify significant differences between treatment means. All statistical analyses were carried out using the Minitab software package 17.

3. Result and Discussion

3.1. Anions
As indicated from table 2 the sulfate content is under risk limit of WHO (3-150 µg/L) in ground water. But there is evidence that a little contamination plume is created in Girresh S6 28.6 µg/L location as shown in figure 2 because it affected directly by point source of industrial effluent and landfill leachate withdrawal comparing with other sites that ranged from 2.6 to 16 µg/L and same findings has
been reported by (Aghazadeh et al. 2010). These low sulfate content in wells water may attributed to the efficiency of soil bacteria especially *Thiobacillus thioxidance* that reduced sulfate ion to elemental sulfur and originally low sulfate content in the soil 0.44 mmole/l as indicated from table 1. The high sulfate concentration in drinking water can cause serious injury to respiratory canal and shows catastrophic effects on human beings health (Sunder et al. 2008).

![Figure 2](image)

**Figure 2.** Concentrations of anions NO$_3$, SO$_4$, and Cl mg/L in ten studied locations

The chloride anions concentration as typical recommended by WHO in ground water is 1-70 mg/L and is in low levels in 5 artesian wells upper north border of industrial area that not significantly affected by effluents and leachates and ranged between 8-12 mg/L as shown in figure 2. These ranges are obviously increased in the rest 5 locations down ward the industrial area that influenced directly by effluent and leachate withdrawal to the south direction as shown in figure 1 and table 2 recording high level in S10 Tobzawa location 38 mg/L indicating that the contamination plume is created in these locations although they yet not reached to risky level but it gives a predicate that the pollution will reach to hazardous levels if the effluents and leachate remain without treatments and solutions. These relatively high concentrations it may attribute to the salt contaminating nature of this location that locates the down-word location of water runoff from Bexer mountain upper industrial area. These results are with agreements with (Balakrishnan et al. 2008). The nitrate anions is probably the most concerned anions associated with drinking water pollution as will known health damaging anions like methemoglobinemia and formation of carcinogenic and mutagenic nitrous amine in gastrointestinal tracts of human being and WHO typical recommended levels of nitrate in ground water is 2-20 mg/L. As a case of chlorine and indicted from figure 2, the concentration of NO$_3$ in S1 to S5 upper industrial area is ranged between 5.1 to 9.7 mg/L and save for drinking and Irrigation. The rest five artesian wells located down ward withdrawal of industrial effluents and landfill leachate are significantly affected toward increasing to reach hazardous levels in three location S8 Sarshour 19.8 mg/L, S7 Marina location 22.7 mg/L and the center of contamination plume risky level pointed in Girrash location of 55.3 mg/L which is not saved for human being uses such as drinking, irrigation and cattle's drinking. Girrash S5 location is more influenced by induced human pollution of Kawshe industrial area in addition to high chemical fertilization of wheat crops by urea in fields around the well as indicated in table 2 and figure 2. Similar results have been obtained by (Sarada 2016).

| Location | SO$_4$ (mg/L) | CL (mg/L) | NO$_3$ (mg/L) | Fe (mg/L) | Cd (mg/L) | Pb (mg/L) | Zn mg/L |
|----------|----------------|-----------|----------------|-----------|-----------|-----------|---------|
| S1       | 4.7            | 0.5       | 4.1            | 0.3       | 0.2       | 0.1       | 0.01    |
| S2       | 7.2            | 1.0       | 6.8            | 0.5       | 0.3       | 0.2       | 0.02    |
| S3       | 9.1            | 1.5       | 8.6            | 0.7       | 0.4       | 0.3       | 0.03    |
| S4       | 11.0           | 2.0       | 10.5           | 0.9       | 0.5       | 0.4       | 0.04    |
| S5       | 14.0           | 3.0       | 13.5           | 1.1       | 0.6       | 0.5       | 0.05    |
| S6       | 17.0           | 4.0       | 16.5           | 1.3       | 0.7       | 0.6       | 0.06    |
| S7       | 22.7           | 5.0       | 22.2           | 1.5       | 0.8       | 0.7       | 0.07    |
| S8       | 38.0           | 6.0       | 37.5           | 1.7       | 0.9       | 0.8       | 0.08    |
| S9       | 55.3           | 7.0       | 54.8           | 1.9       | 1.0       | 1.1       | 0.09    |
| S10      | 80.0           | 8.0       | 79.5           | 2.1       | 1.1       | 1.2       | 0.10    |

*Table 2:* Some anions and heavy metal concentrations mg/L of the studied 10 ground waters and *Summary of ANOVA (P value)*.
Means which do not share a letter in a column are significantly different at probability level of 0.05.

Table 2: Continued.

| Location | Cu mg/L | Cr mg/L | Co mg/L | Mn mg/L | Ni mg/L | Al mg/L |
|----------|---------|---------|---------|---------|---------|---------|
|          | Mean ± SD | Mean ± SD | Mean ± SD | Mean ± SD | Mean ± SD | Mean ± SD |
| Kwashe 1 | 0.376 ± 0.0000001 | ± 0.00017 | ± 0.0766 | ± 0.0165 | ± 0.0069 | ± 0.0000003 |
| Kwashe 2 | 0.225 | ± 0.0000001 | ± 0.0003 | ± 0.0252 | ± 0.0717 | ± 0.0076 |
| Kwashe 3 | 0.272d | ± 0.0000001 | ± 0.0000001d | ± 0.0026 | ± 0.0175 | ± 0.0073 |
| Kwashe 4 | 0.2151 | ± 0.0000001 | ± 0.00015b | ± 0.0416 | ± 0.0089 |
| Kwashe 5 | 0.208f | ± 0.0000001 | ± 0.0000005 | ± 0.0191 | ± 0.0469 |
| Girres | 0.206 | ± 0.0000001 | ± 0.000013 | ± 0.0183 | ± 0.0415 | ± 0.0206 |
| Marina | 0.020g | ± 0.0000001 | ± 0.000001b | ± 0.0177 | ± 0.0177 |
| Moqbel | 0.295 | ± 0.0000001 | ± 0.00041b | ± 0.0183 | ± 0.0443 | ± 0.0145 |
| Sarshou | 0.213 | ± 0.0000001 | ± 0.0000001c | ± 0.0198 | ± 0.0552 | ± 0.0113 |
| Tobsaw | 0.24b | ± 0.0000001 | ± 0.0000009 | ± 0.0176 | ± 0.0442 | ± 0.0116 |
| Typical values | <1 | <1 | <1 | <1 | <1 | <1 |

Summary of ANOVA (P – value)

Means which do not share a letter in a column are significantly different at probability level of 0.05.

3.2. Heavy metals
The all studied heavy metals in ground water in all locations are under the typical international standards for ground water as indicated from table 2 are not affected by huge release of industrial effluents and landfill leachate. And there are a random distribution of heavy metal accumulation in the upper and the dawnward of industrial area with absence of any evidence that toxin plume of heavy metals are created throughout groundwater of the all ten studied artesian wells. These low concentrations of heavy metals in ground water returned to the optimum soil properties as shown in table 1 like the alkaline nature of the soil 7.9 pH, high active/total CaCO₃, 62.62%, high clay content 38.16% with SiCl texture, and presence of relative high alkaline ions such as Ca, Mg, K, Na and anions as bicarbonate, chloride, carbonate that makes the soil solution to be active in rendering most cationic heavy metals non soluble and unavailable for plants absorption and protecting the ground water from there hazardous contamination. But in most cases the accumulation of heavy metals concentrations are more in Kowashe and in Marina compared to the adjacent artesian wells and this not attributed to the discharge of industrial effluents and leachate but returned to the geochemical properties of this two locations that originally contain more heavy metals especially the iron which is more as hundreds. The statistical analysis showed in table 2 that the almost heavy metals have much lower concentrations than typical standard levels of ground water good quality both in (P<0.05) and (P<0.0001) which mean that the contamination by heavy metals are not severe and under risky levels. While in nitrate case is different in both (P<0.05) and (P<0.0001) comparing with other ground waters

4. Conclusions

1- The nitrate contamination have reached to the risky levels according typical international standards for ground water pollution which are Sarshour 19.70 ± 1.45 mg/L, Marina location 22.67 ± 0.85 mg/L and the center of contamination plume risky level recorded in Girrish of 55.33 ± 0.25 mg/L which is not saved for as drinking water for adults and cattle babies according WHO standards.
2- There are evidence that slight plume contamination is created with both sulfate and chloride the downward industrial effluents and leachate withdrawal and are twice in concentration comparing the five upper wells. Although they not reached to risky limits now but will reach in future if the situation remained without solution.
3- There is obvious evidence that the toxin plume of anions especially nitrate is created in Girresh location which carry negative charge and not attracted to soil colloid that carry the same negative charge to be washed easily with seepage to percolate in groundwater. While the accumulation of heavy metal in this wells are very low and save with standard WHO for drinking water., this reflect that the optimum soil chemical and physical properties especially soil PH over 7 and high soil content of both total and active calcium carbonate and clayey nature of soil rendered heavy metal to precipitate and to become an active in the soil, preventing them to reach groundwater.
4- Kwashe industrial area effluents of petroleum refinery, tanning and dyes factories and leachate of a great landfill must be reduced and treated to further contamination of ground water in the future.

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