

Assessment of the Chemical Quality of Water in the Halabja-Sulaimani, Kurdistan Region of Iraq

Dana A. Mohammed Barzinji* and Dilshad G.A. Ganjo¹

School of Agriculture, Soil and Water Science Department, University of Sulaimani, Kurdistan, Iraq

School of Marine Science and Engineering, University of Plymouth, Plymouth PL4 8AA, UK

¹College of Science, University of Salahaddin, Irbil-Kurdistan, Iraq

✉ danasoilwater@inbox.com

Received July 28, 2013; revised and accepted February 10, 2014

Abstract: A study of water pollution was conducted at Halabja-Sulaimani. Water samples were collected from five different locations in a radial manner around and within Halabja town. Water sources included artesian wells, drilled wells and Kahreezes. Before the chlorination and disinfection process, water samples were collected and then chemical and bacteriological analyses were conducted. The field works commenced according to a regular schedule twice per month, starting in June and ending in November 2007. The chemical evaluation of the well waters in the present study based on standards given for drinking water by the World Health Organization guidelines, can be assessed as good-quality; ranging from moderately hard to hard. Saturated by oxygen and healthy with regard to biological oxygen demand. The maximum and minimum of reactive phosphorus, nitrate, nitrite and chloride were 0.05-4.29 mg at P-PO₄ l⁻¹, 0.83-8.40 N-NO₃ l⁻¹ and 1.42-25.16 mg l⁻¹, respectively. All water samples during the investigation period revealed pollution by nickel, lead, molybdenum and chromium. In all investigated sites, cations were dominated by calcium followed by magnesium, sodium and potassium in order of decreasing concentrations.

Key words: Water pollution, Halabja, heavy metal.

Introduction

All existing life forms on Earth depend on water; each human being needs to consume several litres of fresh water daily to sustain life. Over 97% of the world's water is sea water, which is unsuitable for drinking and for most agricultural purposes. Three quarters of the fresh water is trapped in glaciers and icecaps. Lakes and rivers are one of the main sources of drinking water, even though collectively they constitute less than 0.1% of the total water supply. Recently it was estimated that humanity currently consumes, mostly for agriculture, about one-fifth of the accessible runoff water destined for the sea; this fraction is predicted to rise to about three-quarters by 2025. Despite that only 10% of the

world's population in 2000 lived under conditions of water stress or scarcity (Barid and Cann, 2005).

The availability of water supply adequate in terms of both quantity and quality is essential to human existence (Peavy et al., 1985). Ground water, the water that lies hidden beneath the earth's surface, is an important resource. Although it makes up only 4% of the total amount of water on earth, it constitutes 95% of the fresh water that is suitable for human consumption (Gary, 2007). In many countries, where lakes and rivers do not exist, the seasonal ground water is the main source of fresh water. Ground water which is considered a long-term natural reservoir (with residence up to millennia), makes about 0.6% of the fresh water. This amount is by far the most sizable fresh water available for large populations (Koyi, 2007).

*Corresponding Author

One of the strategies of any water quality monitoring programme is providing information on the success or otherwise of water quality assessment parameters to reduce or eliminate pollution. So, it is useful to classify foreign substances in water and soil, such as heavy metals and other physico-chemical variables. All these often determine the effectiveness of various methods of purification. Thus, the main task of agronomists will be interpretation of principles and to show how these principles can be applied to the study of different kinds of freshwater systems.

Within Halabja-Sulaimani province, there is a great abundance of water systems. All these originate in the high mountains and foothills, providing a permanent source of water. So far, there is little information on the pollution in water resources at Halabja town. However, this area suffers from chronic stress (bombarded by chemical weapons in 1988), in addition to huge amounts of agricultural and other human activities for the last three decades. Furthermore, as the number of investigations increase, the limits and expected changes become defined more clearly and valuable baseline data can be established. Moreover, an examination of selected variables over a course of time provides some tentative limits by which to judge past, present, and future events in the system. Therefore, a water pollution study on the Halabja town was conducted with urgency in order to:

- obtain selected data for definition of certain physical and chemical characteristics of water resources at Halabja area,
- determine weather, chemical weapons, natural and human activities affecting the magnitude and changes in magnitude of concerned variables in Halabja, and
- evaluate the present enrichment condition of water resources.

The study comprises physical, chemical and biological characteristics of water, but is divided into two parts. This paper focusses on chemical characteristics of water.

Materials and Methods

Description of the Studied Area

Sulaimani is one of the important large cities of the Kurdistan region of Iraq. Sulaimani district occupies more than 1200 km² in the Kurdistan region of Iraq. Most of the region is high plateau, more than 850 m above sea level, becoming increasingly mountainous towards the Zagros mountain in the north from this

area the large perennial river, the lesser Zab descends eventually draining to the river Tigris. There are also many ephemeral watercourses which become dry during summer; the area bounds with springs and sources of underground water, most of which are used for water supply and irrigation purposes (Maulood and Hinton, 1979).

Halabja is one of the main towns in Sulaimani governorate, at intersection point of longitude (35.1786° N), and latitude (45.9853° E). It is located east of Sulaimani city at a road distance 82 km. Sampling sites are shown in Figure 1.

Sampling Sites and Sample Collection

A broad spectrum of activities for the present research was considered in order to implement this project. For the purpose of the present study water samples were collected from five sampling sites. The selected sites included artesian wells, drilled wells and Kahrezes situated at different locations (in a radial manner) of Halabja town. Water samples (before chlorination and disinfection process) were collected for chemical and bacteriological parameters according to a regular schedule at twice per month interval periods during June to December, 2007. All water samples were collected following instructions recommended by American Public Health Association APHA (1998).

Laboratory Methods

Chemical Characteristics of Water

Alkalinity: It is the measure of the ability of water to neutralize acids. Titration method was used for determination of alkalinity as recommended by Mackerth (1963). Results were expressed in mg CaCO₃ l⁻¹. However, Table 1 recommended by APHA (1998) was used for determination of hydroxide, carbonate, and bicarbonate alkalinity.

$$\text{Alkalinity in mg CaCO}_3\text{l}^{-1} = \frac{A \times B \times 50 \times 1000}{\text{Volume of sample ml}}$$

where A is volume of H₂SO₄ (ml) and B is normality of H₂SO₄.

Acidity: The ability of water to neutralise strong base to a designated pH is called acidity. In the laboratory, titration method was used for determination of acidity (Abbawy and Hassan, 1990). Results were expressed in mg CaCO₃ l⁻¹ using the following equation:

$$\text{Acidity in mg CaCO}_3\text{l}^{-1} = \frac{A \times B \times 5 \times 1000}{\text{Volume of sample ml}}$$

where A is volume of NaOH (ml) and B is normality of NaOH.

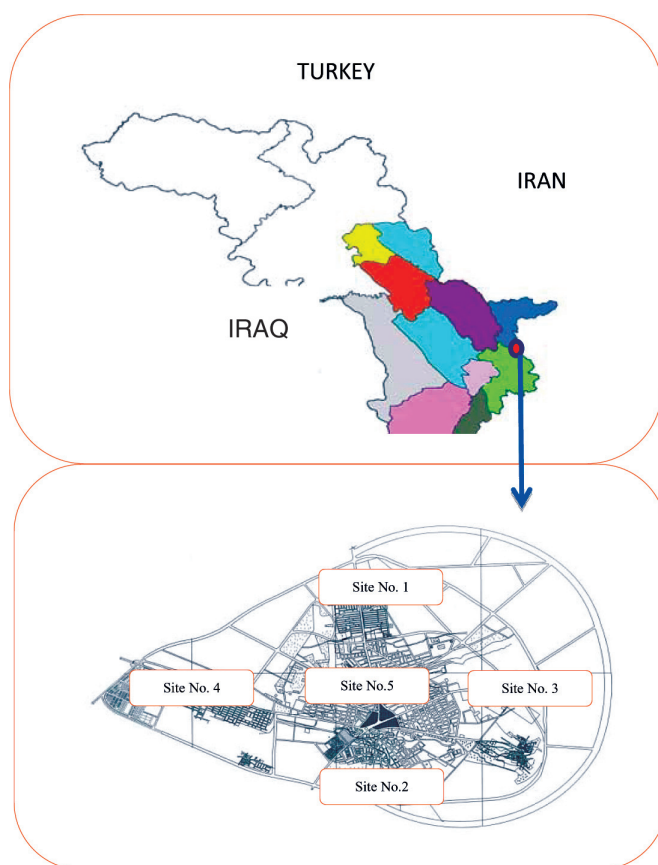


Figure 1: Water sample collection points.

Major Cations

Sodium and Potassium (Na^+ and K^+): Sodium and potassium are relatively abundant elements, and they are present to some extent in most natural waters (Bartram and Balance, 1996). Flame photo-metric method was used as described in APHA (1998) using Corning-400 Flame-photometer-U.K. Sodium and potassium emission readings were taken at wavelength of 589 and 767 nm, respectively. A series of standard stock solutions (0.1 to 8 mg l^{-1}) of Na^+ and K^+ from NaCl and KCl were prepared for calibration of the instrument, and creating calibration curve. Final results were expressed in mg l^{-1} .

Major Anions

Chloride (Cl^-): Agentometric method (Mohor Method) was used for determination of chloride content in water sample. Silver nitrate solution (AgNO_3) as a titrant and potassium chromate (K_2CrO_4) as an indicator were used, as described by Sawyer and MacCarty (1978).

$$\text{Chloride (mg Cl l}^{-1}\text{)} = \frac{(V_1 - V_2) \times N \times 35.45}{\text{Volume of sample} \times 1000}$$

where V_1 is volume of silver nitrate required by the sample (ml), V_2 – volume of silver nitrate required by the blank (ml), N – normality of silver nitrate, and 35.45 is molecular weight of Cl^- .

Total Hardness: An accurate method was used for determination of total hardness and calcium hardness depending on the procedure given by Theroux et al. (2001). The measurements of total hardness were conducted depending on the mathematical model below:

$$\begin{aligned} &(\text{ppm Ca} \times 2.496) + (\text{ppm Mg} \times 4.115) \\ &= \text{ppm Total hardness as CaCO}_3 \end{aligned}$$

Calcium and Magnesium Hardness: The hardness of calcium and magnesium in each water sample was measured and calculated according to these equations outlined by Theroux et al. (2001):

$$(\text{ppm Ca} \times 2.496) = \text{Calcium hardness as CaCO}_3$$

$$(\text{ppm Mg} \times 4.112) = \text{Magnesium hardness as CaCO}_3$$

Major Nutrients

Reactive Phosphorus (PO_4^{3-}): All methods for estimating reactive phosphorus are mainly colorimetric dependence, and most are depended on the formation of a blue colour solution above acidic base. For laboratory, the procedure is described by Parsone et al. (1984). Water samples were allowed to react with a mixed reagent, consisting of ammonium molybdate, ascorbic acid (kept frozen between analysis), concentration of sulphuric acid, and trivalent antimony 1-tartarate solution. The absorbance

Table 1: Determination of hydroxide, carbonate and bicarbonate alkalinity recommended by APHA (1988)

Result of titration	Hydroxide alkalinity as CaCO_3	Carbonate alkalinity as CaCO_3	Bicarbonate alkalinity as CaCO_3
$P = 0$	0	0	T
$P < 1/2 T$	0	$2P$	$T - 2P$
$P = 1/2 T$	0	$2P$	0
$P > 1/2 T$	$2P - T$	$2 (T - P)$	0
$P = T$	T	0	0

P = Phenolphthalein alkalinity

T = Total alkalinity

of this solution was measured spectro-photometrically using UV-VIS. Spectrophotometer (TU.1800, UK), at wavelength of 885 nm. Results were expressed in mg l^{-1} .

Nitrate Nitrogen (NO_3): The nitrate concentration of the water samples were estimated by using a special nitrate-sensitive membrane electrode (Ino lab.pH, Ion, Cond.750-Multiparameter laboratory, WTW, Germany, 2004). The results were expressed in mg l^{-1} .

Nitrite Nitrogen (NO_2): The concentration of nitrite in the water samples were determined spectro-photometrically using photospektral lab. (WTW, Germany, 2004). One micro-spoon (0.2 mg) of nitrite reagent (sulphanilic acid) was added to 5 ml of water sample, shaking vigorously to dissolve the solid substance, then check pH, specific range 2.0-2.5; for adjusting pH use dilute sodium hydroxide or sulphuric acid. After that, leave the solution for 10 minutes for reaction time. The extinction of the solution in 1 cm cuvette was measured at wavelength of 543 nm. The results were expressed in mg l^{-1} .

Heavy Metals: Trace heavy metals in the water

samples were determined by atomic absorption as recommended by APHA (1998). The procedure of in-situation was conducted depending on direct Air-Acetylene (C_2H_2). Flame method following the condition spectro-photometer that was chosen for determination of Co, Cr, Cu, Mo, Ni and Pb was used as shown in Table 2.

A model of atomic absorption spectro-photometer (An Analyst 200-Atomic absorption spectrophotometer-China), Perkins-Elmer (2006), was used for heavy metal determination in water sample (250 ml) and blanks. Five ml of concentrated HNO_3 was added to minimise absorption of the metals on the container wall. Measurements were expressed in mg l^{-1} .

Statistical Analysis

Analysis of variance was carried out using Stat graphic software Release plus 4.0. The mean and the less significant differences (LSD) values of each limnological data were calculated, at probability 99% for both dates and sites. The means of all parameters are presented in Tables 3A and 3B.

Table 2: Wavelength of measured metals

Parameter	Co	Cr	Cu	Mo	Ni	Pb
Wave length (nm)	240.73	357.87	324.8	313.3	232	283.3
Spectral bandwidth (nm)	0.2	0.2	0.2	0.2	0.2	0.2
Lamp current (mA)	10.0	10.0	4.0	6.0	7.0	5.0

Table 3A: Mean of chemical parameters

Parameters/ Station	Ca hardness mg Ca l^{-1}	Mg hardness mg Mg l^{-1}	Alkalinity mg l^{-1}	Acidity mg l^{-1}	Na mg l^{-1}	K mg l^{-1}	Total hardness $\text{mg CaCO}_3 \text{ l}^{-1}$	Chloride mg l^{-1}
1	207.49	41.34	19.8	2.23	1.59	1.07	248.82	13.77
2	279.29	73.2	23.03	2.25	2.83	1.16	352.49	12.09
3	238.18	97.57	22.78	2.06	1.89	1.15	328.24	12.08
4	291.21	48.08	24.36	1.91	2.37	1.15	339.3	15.23
5	250.03	72.55	22.92	1.81	1.94	1.11	322.58	13.21
Mean	253.24	66.55	22.58	2.05	2.12	1.13	318.29	13.28

Table 3B: Mean of chemical parameters

Parameters/ Station	PO_4 mg l^{-1}	Nitrate mg l^{-1}	Nitrite mg l^{-1}	Cobalt mg l^{-1}	Copper mg l^{-1}	Chromium mg l^{-1}	Molybdenum mg l^{-1}	Nickel mg l^{-1}	Lead mg l^{-1}
1	0.31	3.7	0.03	2.25	0.92	2.18	0.23	0.32	0.28
2	1.14	3.3	0.04	2.09	0.96	2.14	0.2	0.4	0.3
3	0.43	2.75	0.05	2.09	0.95	2.11	0.19	0.67	0.23
4	0.37	4	0.06	2.15	0.95	2.05	0.27	0.29	0.31
5	1.08	3.51	0.04	2.13	0.94	2.1	0.15	0.31	0.4
Mean	0.66	3.45	0.05	2.14	0.95	2.12	0.21	0.4	0.3

Results and Discussion

Alkalinity

Alkalinity is an important characteristic of natural and polluted water, in which measurement of potential hydrogen differentiates between their alkalinity or acidity (Hem, 1985).

The minimum level of alkalinity in the studied area was 16.40 mg $\text{CaCO}_3 \text{ l}^{-1}$ recorded from Site 2 in June while the maximum value observed was 29.20 mg $\text{CaCO}_3 \text{ l}^{-1}$ recorded for site 2 during July. The result can be concluded that the variation in alkalinity may be connected with more than one factor, among them dissolved carbon dioxide concentration, microorganism activities, and hydrolysis of bicarbonate ions. Anon (1975) explained that most Iraqi waters are generally dominated by HCO_3^- ions which hydrolyses to give an alkaline solution. Bicarbonates in the feed water act as a major source for carbonate, bicarbonate and hydroxide alkalinity. Carbon dioxide is insoluble in warmer water and so is removed with the hot water. This cause an increase in pH again and a shift in alkalinity forms from bicarbonate to carbonate and from carbonate to hydroxide (Sawyer and MaCarty, 1978).

Acidity

Acidity of water is ability to neutralise strong base to a designated pH. Carbon dioxide is a normal component of all natural water. It may enter surface water by absorption from the atmosphere, but only when the partial pressure of the carbon dioxide in the water is less than this partial pressure of the carbon dioxide in the atmosphere. In accordance with Henry's law, carbon dioxide may also be produced in waters through biological oxidation of organic matter, particularly in polluted water (Sawyer and MaCarty, 1978).

During the period of the study, the acidity levels were clearly fluctuated between studied sites and ranged from 0.84 to 4.39 mg $\text{CaCO}_3 \text{ l}^{-1}$ at site 1 and site 2 during August and September, respectively. The monthly variation in acidity was evident; the spatial variation in acidity in each season is possibly related to the nature of the geological formation. The amount of carbon dioxide in solution has an influence on the alkalinity and pH (Maulood et al., 1978).

Major Cations

Sodium

Sodium is a common element present to some extent in most natural waters. Its concentration varies from negligible in fresh water to considerable in seawater and

brackish water. When combined with certain anions (e.g. chloride), sodium imparts a salty taste to drinking water (Bartram and Balance, 1996). The average abundance of sodium cation in ground water is generally less than 5 mg l^{-1} ; moreover sodium cation consists about 0.02-0.62% of soil and about 2.5% of the earth's crust (APHA, 1998). Most water supplies contain less than 20 mg l^{-1} , but in some countries its level may exceed 250 mg l^{-1} . Saline intrusion, mineral deposits, and sewage effluents can all contribute significant quantities of sodium to water.

An overall mean sodium ion concentration recorded for the present work was 2.12 mg l^{-1} ($n = 60$). The minimum sodium ion concentration was 0.11 mg l^{-1} determined at site 4 during mid-September, while the maximum sodium ion concentration was 5.44 mg l^{-1} measured at site 2 during July. No firm conclusion can be drawn concerning the possible association between sodium in drinking water and the occurrence of hypertension; therefore, no health based guideline value is proposed. However, the maximum permissible concentration of sodium was 250 mg l^{-1} (WHO 2006), whereas according to USEPA (2004) the health-based value was 20 mg l^{-1} . Accordingly, all studied groundwater samples during this investigation were within the desirable concentrations and were in the safe side for drinking purpose.

Potassium

Potassium is slightly less common than sodium and more abundant in sedimentary rocks. Sources of potassium are the principal potassium minerals of silicate rocks, such as mica and microcline (Hem, 1985). It is well known that potassium concentration is less than that of sodium in natural waters (Davis and Dewiest, 1966; Golterman, 1975). Potassium cation occurs in ground water as a result of mineral dissolution, from decomposing plant material, and from agricultural runoff (APHA, 1998). Potassium ion concentration showed an overall mean 1.13 mg l^{-1} ($n = 60$). The minimum potassium ion concentration was 0.59 mg l^{-1} noted at site 1 during mid-October, while the maximum potassium ion concentration was 1.65 mg l^{-1} observed at site 2 during mid-November. Samples revealed lower concentrations of potassium than sodium in accordance to the results obtained in Sulaimani city by Mustafa (2006) and in Hawler city by Chnaray (2003). According to the previously mentioned guideline and standards, and correspondingly the present results, at all studied sites water were within the desirable levels and were in the safe side for drinking water purpose.

Water Hardness

Hardness of water is equivalent to concentration of multivalent metallic cations in solution; at supersaturated conditions, the hardness cations will react with anions in the water to form a solid precipitate (Peavy et al., 1985). Hardness of water can be divided into two kinds; temporary hardness which is due to the presence of bicarbonates of calcium and magnesium and also termed sometimes carbonate hardness. Permanent hardness is due to the presence of sulphates, chlorides and nitrates of calcium and magnesium and is also defined as non-carbonate hardness (Nabi, 2005).

According to Al-Manharawi and Hafiz (1997) increasing hardness of drinking water has a health impact, which causes precipitation of salts in vessels, formation of real stone and pre-mature aging. Increasing hardness of water causes many problems in industry, which lead to precipitation and corrosion in coolers and heaters.

The present results showed the minimum total hardness value ranged from 178.84 to 636.46 mg CaCO_3 l^{-1} , calcium hardness ranged from 144.52 to 516.95 mg CaCO_3 l^{-1} and magnesium hardness was within the range of 5.56-158.97 mg CaCO_3 l^{-1} . Calcium levels were higher than magnesium. According to the data of total hardness, the studied waters were considered to be ranging from moderately hard to hard (Khopkar, 2004). On the other hand, the guideline of WHO (2006) was 500 mg CaCO_3 l^{-1} . Thus, all investigated sites were considered safe for drinking purpose water.

Major Anions

Chloride

Chloride ions are usually present in natural water. It occurs in high concentration in waters that have been in contact with chloride containing geological formations; however normal ground waters contain 10–30 mg l^{-1} (Wetzel, 1975; Bartram and Balance, 1996; Al-Manharawi and Hafiz, 1997). Chloride concentration in studied sites showed an overall mean of 13.28 mg l^{-1} ($n = 60$). The concentration of chloride during this investigation ranged 1.42–25.16 mg l^{-1} at sites 3, 4 and 5 during June and August, respectively. Obvious seasonal variations in chloride ion concentration were observed throughout the entire sampling period. Chloride has no adverse effect on health, but it imparts undesirable taste to drinking water; with increase in level of chloride in water, corrosiveness of metals also increases (Khopkar, 2004). According to WHO (2006), the maximum allowable concentration of chlorides in drinking water

is 600 mg l^{-1} , while the desirable guideline value is 250 mg l^{-1} . Thus, all investigated wells and Kharezee contain desirable chloride concentration and are safe for drinking purpose water.

Major Nutrients

Reactive Phosphorus

Phosphorus is a chemical commonly found in soil, rock and plants. It is an essential nutrient for plants' growth. Ground water rarely contains more than 0.1 mg l^{-1} phosphorus unless they have passed through soil containing phosphate or have been polluted by organic matter (Bartram and Balance, 1996). The phosphorus concentration during the period of this investigation ranged from a 4.29 high to a moderate concentration of 0.05 mg P-PO_4 l^{-1} . This situation has been referred by many authors (Chnaray, 2003; Muhammad, 2004) in Hawler and Sulaimani provinces, respectively. According to Khopkar (2004) who made a comparison list of international drinking water standards, the high levels of phosphorus may be a result of the excessive use of fertilizers such as super-phosphate in the area which lead to increase of phosphate concentrations in ground water. Both phosphate and clay particles have negative charges resulting in passage of the ion through the soil during the rainfalls and recharging aquifers as described and observed by Shekha (2001). However most of the bacterial contaminated wells have greater phosphorus levels than the others. This may be attributed to the PO_4^{-3} and may act as a nutrient source essential for growth of various organisms as described by APHA (1998).

Nitrate Nitrogen

Nitrate is the most highly oxidized form of nitrogen compounds, and is commonly present in surface and ground water since it is the final product of the aerobic decomposition of organic nitrogenous matter (Bartram and Balance, 1996). The balance of nitrate in a water system is strongly depending upon biological processes such as: nitrification, nitrate reduction, denitrification, and autotrophic assimilation (Golterman, 1975; Tebbutt, 1977; Brown, 1989; House, 1994; Mackenzie, 2003). Nitrate concentration in ground water and surface water is normally low, but can reach high levels as a result of leaching or run off from agricultural land or contamination from human activities or animal wastes as a consequence of the oxidation of ammonia and similar sources (WHO, 2006). The main inorganic sources of contamination of drinking water by nitrate are potassium nitrate and ammonium nitrate used mainly as fertilizers.

Nitrate contamination is responsible for several diseases as hypertension, cancer and birth defect (Spalding and Exner, 1993). Generally, the total mean of nitrate calculated from entire sampling period was 3.45 mg l^{-1} as N-NO_3 ($n = 60$). Nitrate nitrogen concentration of all investigated waters ranged from 0.83 to 8.40 mg l^{-1} as N-NO_3 . The lower concentration was recorded from site 2 during October, while the higher concentration was determined at site 4 during mid-November. It was observed that shallow wells are more susceptible to nitrate contamination. Same phenomena have been referred by Nabi (2005) in Hawler province ground waters and Nolan (2001) in United States. High levels of nitrate in drinking water may present a risk to infants because of the low acidity of their stomachs; favours the reduction of nitrate to nitrite by microbial action, then nitrite readily absorbed into blood where it combines irreversibly with haemoglobin to form methaemoglobin which is ineffective as oxygen carrier in the blood (Bartram and Balance, 1996). For this reason WHO (2006) suggested that the maximum contamination level of nitrate in drinking waters should be lower than 50 mg l^{-1} as N-NO_3 .

Nitrite Nitrogen

Nitrite is a naturally occurring ion that is part of the nitrogen cycle. An aerobic condition may result in the formation and persistence of nitrite. The formation of nitrite is as a consequence of microbial activity and may be intermittent. Nitrification and distribution systems of drinking water can increase nitrite levels, usually by 0.2 – 1.5 mg l^{-1} (WHO, 2006). The primary health concern regarding nitrite is the formation of methaemoglobinaemia, so-called “Blue baby syndrome”. Nitrate is reduced to nitrite in the stomach of infants and nitrite is able to oxidize hemoglobin (Hb) to methaemoglobin (met Hb) which is unable to transport oxygen along the body (USEPA, 2004; WHO, 2006). Nitrite nitrogen values were comparatively low during investigation period. However, the total mean of $0.05 \text{ mg l}^{-1} \text{ NO}_2$ ($n = 60$) was recorded for the studied area. On the other hand, nitrite concentration was at low value of $0.01 \text{ mg l}^{-1} \text{ N-NO}_2$ which was frequently recorded from other sites during different times. The higher value of $0.34 \text{ mg l}^{-1} \text{ N-NO}_2$ was recorded for site 4 during June. This wide variations in nitrite concentration can be due to agricultural activities. The concentration of nitrite ion in ground water are rarely found, while in surface water must be less than 0.005 mg l^{-1} . As a result of agricultural activities, the nitrite concentration can easily reach several hundred

milligrams per litre (Butzer, 1958). According to WHO (2006), a provisional guideline value for nitrite in water must not exceed 0.2 mg l^{-1} (Butzer, 1958; Al-Manharawi and Hafiz, 1997).

Heavy Metals

Cobalt

Cobalt concentration in drinking water around the world are normally below $18 \mu\text{g l}^{-1}$ (Gene, 2003). Cobalt and nickel are much less abundant than iron. The estimated occurrence of these two elements in the earth's crust is $1 \times 10^{-5}\%$ and 0.02% , respectively. Cobalt commonly occurs in the form of arsenides or sulphides, generally associated with the corresponding compounds of iron, silver, nickel and copper. Cobalt is not of major industrial importance since the total annual production for the world is less than 10,000 tons (Bartram and Balance, 1996). The cobalt concentration of all investigated waters in the studied sites ranged from 1.17 to 2.74 mg l^{-1} . The lower concentration was recorded at site 2 during October, while the higher concentration was found at site 1 during June.

Copper

Copper is an essential element for plants and animal metabolism; its compounds are widely distributed in nature including surface water and some ground water. It is present in the form of dissolved or insoluble compounds. In water with high concentration of hydrocarbons, copper occurs as Cu^{2+} ions and in the form of complexes (CuSO_3 , $[\text{Cu}(\text{HCO}_3)_2]$, $[\text{Cu}(\text{OH})_3]^-$ and $[\text{Cu}(\text{OH})_4]^{2-}$ (Tesconi, 2000). Copper is considered both as an essential nutrient and drinking-water contaminant and it has many commercial uses. It is used to make pipes, valves and fittings (WHO, 2006).

The minimum copper concentration was 0.52 mg l^{-1} at site 1 during mid-July and the maximum of 0.98 mg l^{-1} at sites 3, 1, 2 and 4 during the period of the study. On the other hand, the maximum acceptable concentration of copper in drinking water depending on WHO and Canada (2006) were 2 mg l^{-1} and 1 mg l^{-1} , respectively. Accordingly, all studied water samples during this investigation were within the desirable quality and were in the safe side for drinking purposes.

Chromium

Chromium occurs in minerals mostly as chrome ion or chromate (FeCr_2O_2), in which it is present as Cr^{3+} . It is generally present at low concentrations in natural waters (USEPA, 2004). Background levels in water typically range between 0.2 and $20 \mu\text{g l}^{-1}$, with an average $1 \mu\text{g l}^{-1}$ (Weiner, 2000). In this investigation, the minimum

concentration of chromium recorded was 1.43 mg l^{-1} at site 4 during August, while the maximum level observed was 2.87 mg l^{-1} at site 3 during November. The harmful effects of chromium to human health are caused by hexavalent chromium, which cause damage to the liver, kidney circulatory, and nerve tissues. All water samples during this investigated period showed pollution by chromium, which exceeded permissible level 0.1 mg l^{-1} that is recommended by USEPA (2005).

Molybdenum

Molybdenum is widely distributed in trace amounts in nature, occurring chiefly as insoluble molybdenite (MoS_2) and soluble molybdates (MoO_4^{-2}) (WHO, 2004). It is relatively mobile in the environment because soluble compounds predominate at $\text{pH} > 5$. Fresh water usually contains less than 1 mg l^{-1} molybdenum. It is an essential trace nutrient for all plants and animals and it is considered non-toxic to humans, but excessive levels (10 mg day^{-1} for a 70 kg adult) may cause high uric acid levels (Weiner, 2000).

The molybdenum levels during this investigation showed fluctuation between studied sites as indicated by data analysis and its value ranged from 0.05 mg l^{-1} at sites 3 and 5 during November and August to 0.60 mg l^{-1} at site 5 during September. Molybdenum concentration in all water samples during this studied period exceeded those that are recommended by WHO (2006) which is equal to 0.07 mg l^{-1} .

Nickel

Nickel represents a moderately abundant element in the rocks of earth crust. Nickel concentration reaches 0.13 mg l^{-1} in ground water of some areas containing nickel ores, while nickel concentration in drinking water may be increased if natural or industrial nickel deposits polluted raw waters when leaching from nickel-chromium plated taps and fitting occurs (WHO, 1999). The minimum concentrations of nickel recorded was 0.12 mg l^{-1} at sites 4, 5 and 1 during different times, while the maximum level observed was 0.91 mg l^{-1} at site 2 during mid-October. Researches indicated that increasing nickel concentrations above 5 ppm in drinking water lead to infection with cancer in different parts of human body (Al-Manharawi and Hafiz, 1997). All water samples during the investigated period showed pollution by nickel, which exceeded permissible level (0.02 mg l^{-1}) that is recommended (WHO, 2006; EU, 2006) which might be as a consequence of leakage of sewage (Allowey and Ayres, 1997).

Lead

Lead is one of the naturally limited occurrence elements. Lead is toxic to both central and peripheral nervous systems, including subencephalopathic neurological and behavioural effects (WHO, 2006). Lead is a general toxicant that accumulates in the skeleton. Infants, children up to six years of age and pregnant women are most susceptible to its adverse health effect (Moore and Ramanoorth, 1984).

The lead concentration of all studied waters in the investigated site ranged from 0.03 to 0.91 mg l^{-1} . The lower concentration was recorded for sites 1 and 5 during June and November. While the higher concentration was found at site 5. Lead concentrations in all investigated water samples during this studied period exceeded those that are recommended by EU, WHO and Canada (2006) which is equal to 0.01 mg l^{-1} . Source of high lead concentration may originate from fuels and oils used for water pumping processes. Similar conclusion were made by Mustafa (2006) in Sulaimani province.

Bacteriological Analysis

Bacteria is considered to be one of the highest population of microorganisms in water. In general, they are not present individually, but as clumps or in association with particles of matter. Bacterial density in the water is influenced by many factors such as: temperature, discharge, organic matter, and the incidence of human or animal pollution (Bartram and Balance, 1996). Coli-form, a group of bacteria, is considered to be the basic indicator of suitability of water for domestic, dietetic and other uses (APHA, 1998). It is referred to be recurred from human and animal intestinal tract; thus much concern is made for this group as fecal pollution of water. They are thermotolerant coli-forms and bacteria of fecal origin, as well as some bacteria that may be isolated from environmental sources (Bartram and Balance, 1996).

Fecal coli-form is widely used to evaluate the quality of waste water effluents, environmental fresh water sources, sea water at bathing beaches, raw water for drinking, water supply and recreational water. Fecal coli-form is a subset group of the total coli-form that originates from the intestinal tract of homothermic animals (WHO, 2006). However, understanding the ecology of indicator bacteria is important when interpreting fecal pollution assessment and developing source detection methodology.

Results of the present study show that most of the bacterial contaminated sites have greater phosphorus levels than the others. This could be related to PO_4^{-3} which may act a nutrient source and is essential for growth of organisms (APHA, 1998).

Conclusions

The conclusions to be made from this study are: the chemical evaluation of the well waters based on standards given for drinking water by the WHO guidelines, can be assessed as good-quality; ranging from moderately hard to hard. Saturated by oxygen and healthy with regard to biological oxygen demand. The minimum and maximum of reactive phosphorus, nitrate, nitrite and chloride were 0.05-4.29 mg at $\text{P-PO}_4 \text{ l}^{-1}$, 0.83-8.40 $\text{N-NO}_3 \text{ l}^{-1}$, 1.42-25.16 mg l^{-1} , respectively. All water samples during the investigation period revealed pollution by nickel, lead, molybedinum and chromium. In all investigated sites, cations were dominated by calcium followed by magnesium, sodium and potassium.

Acknowledgements

Financial assistance provided by Kurdistan Regional Government (KRG) via Ministry of Higher Education and Scientific Research (MHE) and University of Sulaimani-Faculty of Agriculture is fully acknowledged.

References

- Abbawy, S.A. and M.S. Hassan (1990). Practical environmental-engineering water analysis. Ministry of education and Scientific Research. Al-Hikama Publishing House. Mousl Univ.
- Alloway, B.J. and D.C. Ayres (1997). Chemical principles of environmental pollution. Second Edition, Blackie Academic and Professional, Chapman and Hall, London.
- AL-Manharawi, S. and A. Hafiz (1997). Fresh Water: Resources and Quality. Arabic Press. Cairo. (In Arabic.)
- Anon (1975). Contributions on Natural Resources Research, Iraq. UNDP Tech. Rep., Paris.
- A.P.H.A – American Public Health Association, American Water Work Association (A.W.W.A.), and Water Environment Federation (1998). Standard methods for the examination of water and waste water. 20th Edition. A.P.H.A1015, 15th street, NW Washington, DC.
- Bartram, J. and R. Balance (1996). Water quality monitoring. A practical guide to the design and implementation of freshwater quality studies and monitoring programme. United Nation Environmental Programme-UNEP and WHO.E and FN Spon. Chapman and Hall, London. U.K.
- Baird, C. and M. Cann (2005). Environmental Chemistry. Third Edition. W.H. Freeman and Company, New York.
- Brown, A.L. (1989). Freshwater Ecology. Heinemann Education Book, UK, Clay Ltd.Bungay, Suffolk.
- Butzer, K.W. (1958). Quaternary statigraphy and climate in Near East-Bonner Geogr. Abhandl.
- Canada (2006). Guidelines for Canadian drinking water quality. Federal-Provincial, Territorial Committee on drinking water. http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2012-sum_guide-res_recom/index-eng.php.
- Champion, K.M. and R. Stark (2001). The Hydrology and water quality of springs in west-central Florida. Water Quality Monitoring Program. Southwest Florida Water Management District. Retrieved from www.swfw.state.fl.us/ppr/springs.pdf.
- Chnaray, M.A.K. (2003). Hydrology and hydrochemistry of Kapran basin Arbil north of Iraq. Ph.D. Thesis, Univ. of Baghdad, Iraq.
- Davis, S.N and R.J.M. DeWiest (1966). Hydrology. John Wiley and Sons, New York, USA.
- Dowdeswell, W.H. (1984). Ecology, principles and practice. Heinman Education Books, London, UK.
- Dybas, C. (2003). Common water measurements. *USGS Water Resources*, **70(3)**: 300-306.
- EU (2006). European standards. EU's drinking water standards. http://nuclearsafety.gc.ca/pubs_catalogue/uploads/info_0766_e.pdf.
- Gary, K. and Felton (2007). Water, Water Wells, and Water Contamination. <http://extension.umd.edu/publications/pdfs/hw3.pdf>.
- Gene, T.S. (2003). The solar relation within a cloudy atmosphere. *Aquatic Ecology*, **2(5)**: 5-15.
- Ghannoum, M.K., Kenneth, E.M. and H.A.H. Ridha (1981). Techniques for the Microbiological analysis of water. Kuwait University. That El-Salasil Publisher.
- Golterman, H.L. (1975). Physiological Limnology: An approach to the physiology of lake Ecosystem. Elsevier, Amsterdam.
- Hem, J.D. (1985). Study and Interpretation of the Chemical Characteristics of Natural Water. USGS Water Supply Paper 254. <http://pubs.usgs.gov/wsp/wsp2254/pdf/intro.pdf>.
- House, C.H., Broome, S.W. and M.T. Hoover (1994). Treatment of nitrogen and phosphorus by a constructed upland-wetland wastewater treatment system. *Water Sci. Technol.*, **29 (4)**: 177-184.
- Khopkar, S.M. (2004). Environmental pollution monitoring and control. 1st Edition. Indian Institute of Technology, Mumbai, Department of Chemistry. New Age International (P) Ltd., New Delhi.
- Koyi, H. (2007). Ground water as a future source of fresh water in the Kurdistan Region, Iraq. Department of Earth Science, Uppsala University, Sweden.

- Mackerth, F.J.H. (1963). Some methods of water analysis for limnologist. *Freshwater Biol. Assoc.*
- Maulood, B.K. and G.C.F. Hinton (1978). Observation on the algal flora of Sulaimani area: (1) green and blue algae Zanco. **Series A.4(1):** 55-75.
- Maulood, B.K. and G.C.F. Hinton (1979). Tychoplanktonic diatoms from a stenothermal spring in Iraq Kurdistan. *Br. Phycol. J.*, **14**: 175-183.
- Mackenzie (2003). Planktonic green algae in an acidification gradient of nutrient-poor lakes. *Nature*, **141**: 47-64.
- Moore, J.W. and S. Ramamoorth (1984). Heavy Metals in Natural Waters: Applied Monitoring and Impact Assessment. Springer-Verlag, New York.
- Muhammad, S.A.M. (2004). An ecological study on the Aquatic life of Sarchnar spring, Chaq-chaq and Kiliassan streams, Sulaimani, Kurdistan region of Iraq. M.Sc. Thesis, Univ. of Sulaimani.
- Mustafa, O.M.M. (2006). Impact of sewage wastewater on the Environment of Tanjero river and its basin within Sulaimani province, Sulaimanyah, Kurdistan region of Iraq. M.Sc. Thesis. Univ. of Bagdad.
- Nabi, A.Q. (2005). Limnological and bacteriological studies on some well water within Hawler city, Kurdistan region, Iraq. M.Sc. Thesis. University of Salahaddin-Erbil, Iraq.
- Parsone, T.R., Maita, Y. and C.M. Lalli (1984). A manual of chemical and biological methods for sea water analysis. Pergamon Press, Oxford.
- Peavy, S.H., Rowe, D.R. and G.G. Tchobanoglous (1985). Environmental engineering. International edition. McGraw-Hill Book Co., Singapore.
- Sawyer, C.N. and P.L. McCarty (1978). Chemistry for environmental engineering. 3rd Ed. McGraw-Hill. Inc
- Shekha, Y.A. (2001). An Ecological study and Bacteriological study for ground water in Arbil region. *Jour. of Brayati Center*. **18**: 207-221.
- Skidmore, A. (2003). Environmental Modeling with GIS and Remote Sensing. McGraw-Hill Comp., New York.
- Tebbutt, T.H.Y. (1977). Principles of Water Quality Control. Second edition. Pergamon Press, Oxford, UK.
- Tesconi, T. (2000). Water Quality Control. Part III: Human impact on water resources. The Press Democrat.
- Theroux, F.R., Eldridge, E.F. and L.W. Mallmann (2001). Laboratory manual of chemical and bacterial analysis of water and sewage. Chopara, Jodhpur Company Inc.
- USEPA (2004). Edition of the Drinking Water Standards and Health Advisories. Office of Water United States Environmental Protection Agency, Washington, DC.
- USEPA (2005). United States Environmental Protection Agency. Guidelines for Carcinogen Risk Assessment. EPA/630/P-03/001F. Risk Assessment Forum. U.S. Environmental Protection Agency, Washington, D.C.
- Welch. P.S. (1952). Limnological methods. McGraw-Hill Book Company, USA.
- Wetzel, R.G. (1975). Limnology. W.B. Saunders Co., USA.
- Weiner, E.R. (2000). Applications of environmental chemistry: A practical guide for environmental professionals. Lewis Pub. CRC Press, USA.
- WHO (1999). World Health Organization. Guidelines for Drinking Water Quality. 3rd Ed. Vol. 2. Geneva, Switzerland.
- WHO (2004). World Health Organization. Guidelines for Drinking Water Quality. 3rd Ed. Vol. 1, Recommendations. World Health Organization, Geneva.
- WHO (2006). World Health Organization. Guidelines for Drinking Water Quality. 3rd Ed. Vol. 1, Recommendations. Geneva, Switzerland.