

Assessment of Inorganic Chemicals in Groundwater in Rural Provinces of Korea

Jong Yeon Hwang¹, Sunhwa Park, Moon-Su Kim, Hun-Je Jo, Gyong-Mi Lee, Sang Ho Jeon,
Da Hee Song, Deok-Hyun Kim, Tae-Seung Kim, Hyen Mi Chung, and Hyun-Koo Kim[†]

¹Soil and Groundwater Research Division, National Institute of Environmental Research, Incheon 22689, Korea

Received June 16, 2017/Revised June 21, 2017/Accepted June 23, 2017

In this study, we focused on the evaluation, comparison of the physiochemical characteristics, and distribution of cations and anions in groundwater sampled in rural areas of Korea. The on-site measurements of pH, EC, DO, and ORP (average, minimum, and maximum) respectively ranged as follows: 5.7~8.7, 49~1,224 $\mu\text{S}/\text{cm}$, 0.5~11.8 mg/L, and -53.0~697 mV. The assessments of water quality for agricultural usages were evaluated using SAR, sodium (%), RSC, PI, SSP, MH, PS, and Kelly's ratio (KR) and were classified as SAR [Excellent (100%)], Sodium [Excellent (2.1%), Good (51.1%), Permissible (39.3%), Doubtful (6.2%), Unsuitable (0.7%)], RSC [Good (100%)], PI [Excellent (100%)], SSP [Excellent (0.7%), Good (37.2%), Fair (61.4%), Poor (0.7%)], MH [Acceptable (96.6%), Non-Acceptable (3.4%)], KR [Permissible (69.7%), (Non-Permissible (30.3%)), and PS [Excellent to Good (100%)]. In addition, classifications of groundwater based on the Piper diagram showed that the groundwater was grouped into the Ca^{2+} -(Cl^- - NO_3^-) and Ca^{2+} - HCO_3^- types, which are general features of groundwater in Korea. Moreover, the tracking of dominance types (classified as evaporation, rock, and precipitation) based on the Gibbs diagram showed that the origins of anions and cations in the groundwater are of rock dominance.

Key words: Groundwater, Geochemical characteristics, Piper diagram, Gibbs diagram, Wilcox diagram, US salinity laboratory diagram, Chadha diagram

1. Introduction

The major inorganic constituents of water originate when water in the form of precipitation dissolves atmospheric gases such as carbon dioxide and reacts with minerals on the earth's surface; this process is called weathering. When groundwater moves down gradient from its recharge area to discharge, other minerals are dissolved, some are possibly precipitated, and other various chemical reactions may occur. Leachate may eventually enter groundwater or run off as surface water. In this process, the chemical constituents of groundwater have been influenced by the mobility of groundwater and physical factors such as pH, ORP, DO, and temperature. Therefore, studying the phy-

sical characteristics and chemical moieties of groundwater have become important divisions of groundwater research in order to extend understanding of groundwater. Thus, in this study, the appropriateness of groundwater qualities for specific purposes based on laboratory-scale chemical analyses and classification of groundwater through comparison of distribution of cations and anions were the focus. Finally, we traced the source of groundwater cations and anions in samples from rural provinces in Korea. Generally, for the classification of groundwater qualities, some mathematical equations are applied for the assessment of water quality of groundwater for specific purposes. We used equations for SAR (Sodium Adsorption Ratio), Na (%), RSC (Residual Sodium Carbonate), PI (Perme-

[†]To whom correspondence should be addressed.

ability Index), SSP (Soluble Sodium Percent), MH (Magnesium Hazard), KR (Kelly's Ratio), and PS (Potential soil Salinity) (M. Vasanthavigar (2012)¹, Abdul Hameed (2010)², S. R. Barick (2014)³, Shubhara Singh (2015)⁴, E. A. Kaka (2011)⁵, Cha-kra-borty B. (2012)⁶, Yinusa A. (2013)⁷, B. S. Badmus (2014)⁸, Radhey Shyam (2011)⁹, Gabriel I. (2011)¹⁰, J. M. Ishaku (2011)¹¹). A Wilcox diagram (Wilcox, 1955)¹² based on Na (%) and electrical conductivity as well as the U.S. Salinity Laboratory diagram (Richards, 1954)¹³ based on SAR and electrical conductivity (EC) were also used to evaluate groundwater quality for agricultural usages. Meanwhile, the Piper diagram method (Piper, 1953)¹⁴, which reflects various distribution patterns of ions in groundwater including anions and cations, was used to track the ionic sources dissolved in the groundwater, and the Gibbs (1970)¹⁵ and D. K. Chadha (1999)¹⁶ diagram methods were applied for tracking ionic sources in the groundwater. Gibbs (1970) proposed the Gibbs diagram based on the correlation between cations and TDS along with the correlation between anions and TDS to track the origin of cations and anions in groundwater. D. K. Chadha (1999) proposed a new form of diagram and showed that newly proposed methods for the determinations of groundwater corresponded well with the classification based on the Piper diagram. B. R. Scanlon (1990)¹⁷ classified groundwater using TDS and cation distribution. Origin tracing of ions in groundwater is also an important area of research. K. Srinivasamoorthy (2014) et al.¹⁸ studied the type of rocks dissolved in groundwater in the Tamiladu region of India, and N. Subba Rao (2002)¹⁹ studied the origin of certain chemical species by comparing the physiochemical factors, such as SiO₂, of groundwater in the Guntur region in India. Nosrat (2010)²⁰, Nandimandalam Janardhana Raju (2014)²¹, and Krishna Kumar (2014) et al.²² carried out studies to identify the ion exchange mechanism using the distribution ratio of cations (Na⁺, K⁺) to anions (Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻, NO₃⁻). Meanwhile, E. Lakshmanan

(2003) et al.²³ also carried out studies to identify whether the origin of ions in groundwater is carbonate minerals or silica minerals using the relative ratio of cations (Ca²⁺, Mg²⁺) to anions (HCO₃⁻, SO₄²⁻). As mentioned earlier in the Introduction, we evaluate the quality of groundwater samples in pre-monsoon and post-monsoon periods from rural areas of Korea using various evaluation methods and classified the groundwater using the Piper diagram. Finally, the tracking methods for assuming the origins of cations and anions dissolved in groundwater were applied by using the Gibbs diagram and the Chadha diagram.

2. Methods

2.1. Sampling preparation and measurement of on-site items

Advancements in technologies and resultant analytical capabilities of laboratories have been realized for the handling, preparation, and analysis of groundwater samples. Because of the special properties of groundwater samples, representative samples from sampling sites or wells may indicate different things to different investigations, mainly because of differing project objectives. Therefore, samples collected after pumping a significant volume of water from the well may be considered representatives of groundwater, whereas samples collected using methods designed to focus on a specific purpose. Therefore, many investigators have acknowledged the difficulty of obtaining samples that are truly representative of subsurface conditions. Because of the importance for "the least disturbance or change in the chemical and physical properties" of water samples, we followed the guideline for groundwater sampling and in situ measurement for on-site items. Samples were collected during the two different seasons of PRe-Monsoon (PRM; June) and POst-Monsoon (POM; July–November) to broadly cover the seasonal variations. A total of 145 (pre-monsoon: 37 samples, post-monsoon: 108 samples) groundwater samples were collected in one-liter sample bottles

that had been acid washed, well-rinsed low-density polyethylene bottles with inside stopper from bore wells and analyzed following chemical parameter guidelines. The samples were collected after sufficiently pumping the wells for 15~20 min and subsequently filtered through 0.45 μm membranes. The analyzed parameters included the activity of hydrogen ion concentration (pH); electrical conductivity (EC); total hardness (TH); total dissolved solids (TDS); cation groups such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+); and anion groups such as bicarbonate (HCO_3^-), chloride (Cl^-), nitrate (NO_3^-), and phosphate (PO_4^{3-}). The pH and EC were measured using pH and EC meters. All anions and cations were analyzed via ion chromatography (Dionex). The analytical conditions of anions and cations in the groundwater are shown in Table 1. Following the guidelines, quality control and quality assurance procedures, such as calibration curves, sample blanks, sample preservation, duplicate samples, standards, and charge balances of ionic substances, were undertaken at every step to avoid the effect of miscellaneous factors.

2.2. Chemical analyses

Just as the methods for the sampling of groundwater are important factors, so, too, is the selection of appropriate analytical method, which is determined based on the purpose and objectives of the investigation. After establishing the purpose and analytical methods, an investigator must select the appropriate analytical methods for the parameters of interest. In this study, the analysis of cations and anions was carried out using a DX-500 Ion Chromatography System from Dionex, with an Ionpac A CS12A column for cation analysis and an

Ionpac AS12A column for anion analysis. Pretests were carried out repeatedly to confirm the value presented via the standard test method in order to verify the precision and accuracy of each analysis. The analytical conditions for cations and anions using ion chromatography are shown in Table 1. The alkali hydroxides (OH^-), carbonates (CO_3^{2-}), and bicarbonates (HCO_3^-) were converted to a calcium carbonate (CaCO_3) concentration for the alkalinity determination. Phosphate levels were determined using the test method for phosphates described in the Standard Chemical Analysis Guidelines for Water and Wastes ES 04360.2 in Korea²⁴, which is based on the optical absorbance at the 880 nm wavelength caused by a mixture of an ammonium molybdate solution and an ascorbic acid solution.

2.3. Evaluation of groundwater for agricultural use

The focus of the application of the classification equations was considered based on the major factors of 1) the total concentration of soluble salts, 2) the relative proportion of sodium to the other cations, 3) the bicarbonate concentration in relation to the concentration of calcium and magnesium, and 4) the concentration of specific elements and compounds. In most irrigation situations, the primary water quality concern is salinity level, as salts can affect both the soil structure and crop yield. However, a number of trace elements may be found in water, which can limit its use for irrigation. As we mentioned, irrigation water pumped from wells contain considerable chemical constituents derived from the natural soil environment and anthropogenic activities that may influence crop yield and soil fertilities. The irrigation of rice paddies and

Table 1. Analytical conditions for measuring anions and cations in the groundwater

	Anions	Cations
Column	IonPac AS12A (25 cm length), 4 mm \times 250 mm	IonPac CS12A, 4 mm \times 250 mm
Eluent	3.5 mM sodium carbonate + 1.0 mM sodium bicarbonate	Methanesulfonic acid 20 mM
Velocity of eluent	1.2 mL/min	1.0 mL/min
Injection volume	50 μL	50 μL
Detector	Electrical conductivity detector	Electrical conductivity detector

farm fields with groundwater always introduces major nutrients and salts into the root zone. Plant roots naturally take up the water but absorb very little salt from the soil solution. Similarly, water evaporates from the soil surface but salts remain behind. These processes result in a gradual accumulation of salts in the root zone, which affects the plants by creating salinity hazard, water deficiency, and toxicity. To develop solutions for mitigating such problems, it is necessary to have logical and scientific understanding of the quality of irrigation water and its effect on soils and crops. From this point of view, in this study, we focused on the properties and suitability of groundwater for irrigation of farm fields and rice paddies, with most of the sampling sites located in the rural areas of the middle and southern provinces of Korea. Hence, major assessment equations for groundwater quality assurance were applied for key items such as SAR, Na (%), RSC, PI, SSP, MH, KR, and PS; all equations applied are shown in Table 2.

2.4. Classification and estimation of groundwater origin

The distributions of cations and anions in groundwater represent the vulnerable physicochemical characteristics caused by the groundwater's interaction with soil or rock while flowing in the aquifer. The aquifer represents the characteristics of water bodies with different chemical compositions formed through

its flow path from main aquifer to soil layers. Thus, the elemental compositions of groundwater are called the hydrochemical facies of groundwater, which are regarded as an important component for the classification and evaluation of groundwater. Many calculation and graphic models have been applied via Piper and Gibbs diagrams. In this study, we used the Piper diagram, which is a major method for classifying groundwater, to classify the samples per sampling period and per purpose for the groundwater. In addition, the distribution of anions (Cl^- , HCO_3^-) and cations (Na^+ , Ca^{2+}) as well as TDS were applied to generate the Gibbs diagram in order to guess the dominance type: evaporation dominance, rock dominance, or precipitation dominance. Besides the Piper and Gibbs diagrams, the Chadha diagram was applied to compare it with the Piper diagram and to determine whether it matched well with the Piper diagram in order to look at the possibility of replacing the Piper diagram.

2.4.1. Piper diagram

Piper diagrams are a combination of anion and cation triangles that lie on a common baseline. Adjacent sides of two triangles are 60° apart. A diamond shape between them is used to replot the analyses as circles whose area are proportional to their TDS. The position of an analysis that is plotted on a Piper diagram can be used to make a tentative conclusion as to the origin of the water

Table 2. Equations and classifications for evaluating the groundwater

	Equation	Classifications	Reference
SAR	$[(\text{Na}^+) / \sqrt{[(\text{Ca}^{2+} + \text{Mg}^{2+}) / 2]}]$	Excellent, Good, Permissible, Doubtful	Richards (1954) ²⁵⁾
Na (%)	$[(\text{Na}^+ + \text{K}^+) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+)] \times 100$	Excellent, Good, Permissible, Doubtful, Unsuitable	Wilcox (1955) ¹²⁾
RSC	$(\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+})$	Good, Medium, Bad	Richards (1954) ²⁵⁾
PI	$[(\text{Na}^+ + \sqrt{\text{HCO}_3^-}) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)] \times 100$	Excellent, Good, Unsuitable	Doneen (1964) ²⁶⁾
SSP	$[(\text{Na}^+ + \text{K}^+) / (\text{K}^+ + \text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})] \times 100$	Excellent, Good, Fair, Poor	Joshi (2009) ²⁷⁾
MH	$[\text{Mg}^{2+} / (\text{Ca}^{2+} + \text{Mg}^{2+})] \times 100$	Suitable, Unsuitable	Paliwal (1972) ²⁸⁾
KR	$\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})$	Permissible, Non-Permissible	Kelly (1963) ²⁹⁾
PS	$\text{Cl}^- + \sqrt{\text{SO}_4^{2-}}$	Excellent to Good, Good to Injurious, Injurious to Unsatisfactory	Doneen (1954) ³⁰⁾

represented by that analysis.

2.4.2. Gibbs diagram

Gibbs diagrams are used to interpret the effect of the hydrogeochemical processes of precipitation, rock-water interaction, and evaporation on groundwater geochemistry. The reaction between groundwater and aquifer minerals has a significant role in groundwater quality, which is useful to assume the genesis of inorganic ions of the groundwater. The Gibbs ratio is calculated using the following equations.

$$\begin{aligned} &\text{Gibbs ratio I (for anions)} \\ &= (\text{Cl}^-) / (\text{Cl}^- + \text{HCO}_3^-) \end{aligned} \quad (1)$$

$$\begin{aligned} &\text{Gibbs ratio II (for cations)} \\ &= (\text{Na}^+ + \text{K}^+) / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}) \end{aligned} \quad (2)$$

2.4.3. Chadha diagram

A Chadha diagram is a somewhat modified version of the Piper diagram and the expanded Durov diagram. The difference in milliequivalent percentage between alkaline earth metals (calcium plus magnesium) and alkali metals (sodium plus potassium), expressed as percentage reacting values, is plotted on the x -axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate plus bicarbonate) and strong acidic anions (chloride plus sulfate) is plotted on the y -axis. The milliequivalent percentage differences between alkaline earth and alkali metals and between weak acidic anions and strong acidic anions would plot in one of the four possible subfields of the proposed diagram.

3. Results and discussion

3.1. Chemical parameters of groundwater

As with all other components of environmental investigation, it is necessary to monitor the effectiveness of decontamination protocols to verify that the contaminants of concern are removed from all

monitoring equipment being decontaminated so that any data generated from samples collected for chemical analysis during the investigation can be considered valid and uncompromised. The common physical parameters measured in the field at the time of sampling were pH, EC, DO, and Eh; these parameters provided useful and preliminary information of the area. To compare the on-site factors per usage and variation pattern of sampling periods, groundwater samples were classified based on their use as agricultural, living, and drinking water and as pre-monsoon and post-monsoon based on the sampling period. Groundwater is generally colorless and odorless and its taste varies according to variation of physical factors. The pH of water, a very important indicator of its quality, is controlled by the amount of dissolved carbon dioxide, carbonates, and bicarbonates. Addition of salts to groundwater may cause a rapid rise in pH, and CaCO_3 increases the pH of water, making it alkaline (Magdy H.El-sayed, 2012)³¹. pH decreases with increasing salinity. In Korea, the pH values of groundwater samples are within permissible limits: 5.8~8.5 for living water, 6.0~8.5 for agricultural water, and 5.0~9.0. In this study, all pH values were well suited for the regulation of pH conditions of the groundwater for its usages. The EC of groundwater from the study area ranged from 49 to 1,224 $\mu\text{S}/\text{cm}$, with a mean value of 294 $\mu\text{S}/\text{cm}$. The spatial variations of EC in June 2016 and November 2016 are listed in Table 3. The groundwater in all sampling site are not shown the salinity in nature and this is due to the sampling site as isolated patches far from the sea. Moreover, there is not much difference between the EC values of pre-monsoon 2016 and post-monsoon 2016. In particular, the EC ranges of living water were narrower than any other water groups, thus we concluded that in the living water more less inorganic contents were dissolved in the living water groups. DO is an important factor for defining groundwater quality, but, in the law for the preservation of groundwater in Korea, the minimum limit for DO (mg/L) for gro-

Table 3. pH, EC, DO, and ORP values (Average, Minimum, Maximum) of samples

Usage		pH			EC ($\mu\text{S}/\text{cm}$)			DO (mg/L)			ORP (mV)		
		Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.
Jun. (n=37)	Agricultural	7.0	6.1	7.9	412	123	1224	3.8	0.7	8.9	187.5	-9.0	456.0
	Living	6.6	6.5	6.8	432	401	462	0.6	0.5	0.8	146.4	82.8	210.0
	Drinking	6.8	5.8	7.8	389	109	811	6.7	0.6	10.8	194.5	86.0	280.0
	Ave.	6.9	5.8	7.9	407	109	1224	4.4	0.5	10.8	187.2	-9.0	456.0
Jul. (n=28)	Agricultural	7.0	6.3	8.0	445	209	1108	5.0	1.8	8.1	2512.6	-26.6	358.6
	Living	7.0	6.9	7.1	414	399	429	1.9	1.9	1.9	139.5	81.5	197.4
	Drinking	6.9	6.4	8.7	359	117	718	6.7	2.2	9.4	232.4	92.0	381.0
	Ave.	7.0	6.3	8.7	412	117	1108	5.4	1.8	9.4	214.5	-26.6	381.0
Sep. (n=59)	Agricultural	7.1	5.8	8.2	139	49	321	4.9	0.7	8.6	328.5	-131.0	697.0
	Living	7.3	7.3	7.4	77	67	86	6.8	6.0	7.5	435.0	357.0	513.0
	Drinking	7.1	6.2	8.0	164	56	292	7.1	2.9	11.8	261.0	-53.0	653.0
	Ave.	7.1	5.8	8.2	151	49	321	6.3	0.7	11.8	292.1	-53.0	697.0
Oct. (n=11)	Agricultural	6.6	6.3	7.1	365	337	411	4.1	2.1	6.8	302.5	217.0	342.0
	Living	-	-	-	-	-	-	-	-	-	-	-	-
	Drinking	6.1	5.7	6.6	366	352	379	6.8	2.8	11.1	293.4	102.0	653.0
	Ave.	6.3	5.7	7.1	366	337	411	5.8	2.1	11.1	296.7	102.0	653.0
Nov. (n=10)	Agricultural	6.9	6.6	7.4	380	220	659	2.4	1.8	3.2	383.0	333.0	424.0
	Living	-	-	-	-	-	-	-	-	-	-	-	-
	Drinking	6.8	6.3	7.6	263	103	569	5.5	2.6	10.1	363.2	331.0	389.0
	Ave.	6.8	6.3	7.6	310	103	659	4.3	1.8	10.1	15.4	13.2	17.8
Usage (n=145)	Agricultural	7.0	5.8	8.2	330	49	1224	4.4	0.7	8.9	254.4	-26.6	697.0
	Living	7.0	6.5	7.4	307	67	462	3.1	0.5	7.5	240.3	81.6	513.0
	Drinking	6.9	5.7	8.7	255	56	811	6.8	0.6	11.8	259.3	-53.0	653.0
	Ave.	6.9	5.7	8.7	294	49	1224	5.5	0.5	11.8	256.1	-53.0	697.0
Seasonal (n=145)	Pre-monsoon	6.9	5.8	7.9	407	109	1224	4.4	0.5	10.8	187.2	-9.0	456.0
	Post-monsoon	7.0	5.7	8.7	250	49	1108	6.0	0.7	11.8	270.4	-53.0	697.0

undwater used in agriculture is not stipulated as a regulatory article. DO (mg/L) in the usage groups of this study are shown in Table 3. The variation patterns of groundwater were as follows: 0.7~8.9 mg/L in agricultural, 0.5~7.5 mg/L in living, and 0.6~11.8 mg/L in drinking waters and seasonal variations from pre-monsoon to post-monsoon periods were 0.5~10.8 mg/L and 0.7~11.8 mg/L , respectively. Reduction potentials (also known as redox potentials) are measurement tools for the tendency of a chemical species for acquiring electrons, thus being reduced. In aqueous solutions, reduction potential is a measurement of the ability of a solution to either gain or lose electrons when it is subjected to change via introduction of a new chemical species. Oxidation/reduction (redox) reaction potential of groundwater (Eh) plays an important

role in the geochemical processes that occur in groundwater. Redox is defined as the transfer of the electrons. Redox reactions are enormously important in aqueous environmental geochemistry. Eh measurements are useful in identifying the redox zones; its value decreases with increases in residence time (Champ et al., 1979)³². Eh values above 300 mV indicate that sulfate is stable in a sampling area because it means that a rechargeable groundwater or surface water could be refilled through the soil layer and subsoil flow. The measurement results of ORP in mV in the groundwater groups produced the following patterns: -26.6~697 mV in agricultural, 81.6~513.0 mV in living, and -53.0~653.0 mV in drinking waters and seasonal variations from pre-monsoon to post-monsoon were -9.0~465.0 mV and -53.0~697.0 mV, respectively. From

the ORP results (Table 3), it could be inferred that the ORP of agricultural areas was wider in range than those of the other samples because inflow of contaminant sources from agricultural activities and local pollution affected the groundwater quality in the agricultural area.

3.2. Major ion chemistry

A wide range of different elements can be dissolved in groundwater as a result of interactions with the atmosphere, surficial environment, soil, and bedrock. Therefore, groundwater tends to have much higher concentrations of most constituents than do surface waters, and deep groundwater that has been in contact with rock for a long time tends to have higher concentrations than shallow or young waters do. In geology and soil chemistry, the major dissolved components of groundwater include cations, such as sodium, magnesium, and potassium, and anions, such as bicarbonate, chloride, and sulfate; these are generally called the major ions. These constituents are typically present at concentrations in the range of a few mg/L to several hundred mg/L. Water moving through the ground will react to varying degrees with the surrounding minerals, and these rock-water interactions give the water its intrinsic chemical properties. Except for the major ions, the silicate minerals that comprise most rocks do not react readily with most groundwater, but carbonate minerals do react quite readily with water and play an important role in the evolution of chemical and physical properties of groundwater. Many of the microscale solutes are dissolved in groundwater in less than 1 mg/L concentrations under natural conditions. The ranges of concentrations of major ions in the groundwater of

lude cations, such as sodium, magnesium, and potassium, and anions, such as bicarbonate, chloride, and sulfate; these are generally called the major ions. These constituents are typically present at concentrations in the range of a few mg/L to several hundred mg/L. Water moving through the ground will react to varying degrees with the surrounding minerals, and these rock-water interactions give the water its intrinsic chemical properties. Except for the major ions, the silicate minerals that comprise most rocks do not react readily with most groundwater, but carbonate minerals do react quite readily with water and play an important role in the evolution of chemical and physical properties of groundwater. Many of the microscale solutes are dissolved in groundwater in less than 1 mg/L concentrations under natural conditions. The ranges of concentrations of major ions in the groundwater of

Table 4. Na⁺, Ca²⁺, K⁺, and Mg²⁺ values (Average, Minimum, Maximum) of samples (mg/L, n=145)

Usage	Cation	Na ⁺			Ca ²⁺			K ⁺			Mg ²⁺		
		Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.
Jun. (n=37)	Agricultural	23.1	7.8	105.3	37.4	11.8	115.8	2.7	0.0	12.1	7.9	1.7	17.3
	Living	20.1	18.0	22.3	41.7	39.6	43.7	3.0	1.2	4.7	11.2	6.3	16.1
	Drinking	19.7	6.3	36.1	37.5	11.1	118.4	7.7	0.5	37.7	7.0	2.2	13.8
	Ave.	22.0	6.3	105.3	37.6	11.1	118.4	4.1	0.0	37.7	7.8	1.7	17.3
Jul. (n=28)	Agricultural	29.1	8.4	112.8	48.4	15.3	124.4	3.9	0.9	12.1	10.3	3.1	18.9
	Living	21.4	18.9	24.0	47.7	47.2	48.2	3.8	1.8	5.7	12.4	7.6	17.1
	Drinking	20.0	5.4	38.3	37.9	12.0	121.4	8.5	0.9	38.1	7.3	3.0	13.8
	Ave.	25.3	5.4	112.8	44.6	12.0	124.4	5.5	0.9	38.1	9.4	3.0	18.9
Sep. (n=59)	Agricultural	23.9	5.1	71.7	36.8	8.7	73.1	3.0	0.5	17.9	7.2	1.9	17.9
	Living	21.0	14.1	27.9	42.1	39.0	45.1	1.6	1.0	2.1	11.1	8.7	13.4
	Drinking	15.7	5.3	40.9	30.1	5.7	108.8	2.1	0.1	33.6	6.1	1.0	25.0
	Ave.	18.9	5.1	71.7	33.0	5.7	108.8	2.4	0.1	33.6	6.6	1.0	25.0
Oct. (n=11)	Agricultural	17.3	12.3	23.6	35.2	9.7	54.9	5.3	0.8	12.2	7.3	4.2	11.3
	Living	-	-	-	-	-	-	-	-	-	-	-	-
	Drinking	13.2	4.6	23.4	37.4	12.6	112.6	7.1	1.1	34.9	5.3	2.5	11.8
	Ave.	14.7	4.6	23.6	36.6	9.7	112.6	6.4	0.8	34.9	6.0	2.5	11.8
Nov. (n=10)	Agricultural	18.3	12.5	23.7	48.0	9.7	111.6	5.5	1.4	11.9	9.1	6.7	11.6
	Living	-	-	-	-	-	-	-	-	-	-	-	-
	Drinking	11.5	4.5	18.9	24.1	13.3	52.0	7.6	1.2	32.6	4.3	2.6	7.5
	Ave.	14.2	4.5	23.7	33.7	9.7	111.6	6.7	1.2	32.6	6.2	2.6	11.6
Usage (n=145)	Agricultural	24.1	5.1	112.8	40.2	8.7	124.4	3.4	0.0	17.9	8.2	1.7	18.9
	Living	20.9	14.1	27.9	43.8	39.0	48.2	2.8	1.0	5.7	11.5	6.3	17.1
	Drinking	16.3	4.5	40.9	32.6	5.7	121.4	4.8	0.1	38.1	6.2	1.0	25.0
	Ave.	20.3	4.5	112.8	36.7	5.2	124.4	4.0	0.0	38.1	7.4	1.0	25.0
Seasonal (n=145)	Pre-monsoon	22.0	6.3	105.3	37.6	11.1	118.4	4.1	0.0	37.7	7.8	1.7	17.3
	Post-monsoon	20.3	4.6	112.8	36.7	5.7	124.4	3.8	0.1	38.1	7.4	1.0	25.0

the study area are given in Table 4 for cations and Table 5 for anions. The concentrations of dissolved major cations and anions in the groundwater vary slightly both regionally and seasonally. The general order of dominance of cations was $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ and for anions $\text{HCO}_3^{2-} > \text{Cl}^- > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{PO}_4^{2-}$ were the dominant ions present in the groundwater samples. In regards to seasonal variations of major ions, groundwater quality will change because of the variation in rainfall recharge, exploitation of groundwater, variation in land use, irrigation return flow, geochemical reactions, and geological formations. These factors play a major role in the seasonal variation of ionic composition in groundwater in the study area. The composition of the infiltrating rainwater depends on the frequency of rainfall, soil environment, agriculture pattern, and thickness of vadose zone.

Sodium ions were the dominant cation of the study samples, and their average concentrations varied from 4.5 to 112.8 mg/L. Sodium, among the alkali metals, is a predominant chemical constituent of natural water. Calcium is a common and widespread element that is distributed widely in soils and rocks. Calcium is the second dominant cation in the groundwater of this region, with average concentrations ranging from 5.2 to 124.4 mg/L. In general, groundwater in hard rock regions has a higher concentration of calcium. Potassium ranged from 0.0 to 38.1 mg/L, and magnesium concentration ranged from 1.0 to 25.0 mg/L, with a mean value of 28 mg/L. The magnesium ion concentrations of the groundwater samples did not vary much compared to those of the other ions. In addition, concerning seasonal variation, all major cationic values of the post-monsoon period were higher than those of the

Table 5. Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , and PO_4^{2-} values (Average, Minimum, Maximum) of samples (mg/L, n=145)

Usage	Anion	Cl^-			SO_4^{2-}			CO_3^{2-}			HCO_3^-			PO_4^{3-}		
		Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.
Jun. (n=37)	Agricultural	32.0	7.0	160.0	19.9	2.5	57.2	52.0	24.0	140.4	105.6	48.7	285.2	0.0	0.0	0.4
	Living	40.0	34.0	45.0	25.9	23.6	28.1	55.8	39.6	72.0	113.3	80.5	146.2	0.0	0.0	0.0
	Drinking	32.0	5.0	58.0	16.9	0.0	37.7	38.5	15.6	129.6	78.2	31.7	263.1	0.0	0.0	0.0
	Ave.	32.0	5.0	160.0	19.4	0.0	57.2	48.6	15.6	140.4	98.6	31.7	285.2	0.0	0.0	0.4
Jul. (n=28)	Agricultural	38.0	6.0	167.0	21.7	1.6	60.8	55.8	18.0	139.0	113.2	36.6	282.3	0.1	0.0	0.6
	Living	33.0	32.0	34.0	29.8	25.1	34.5	56.6	30.6	82.6	114.9	62.1	167.8	0.0	0.0	0.0
	Drinking	29.0	5.0	56.0	14.4	1.4	33.9	33.0	10.8	131.4	67.1	21.9	266.9	0.0	0.0	0.1
	Ave.	34.0	5.0	167.0	19.7	1.4	60.8	47.7	10.8	139.0	96.9	21.9	282.3	0.0	0.0	0.6
Sep. (n=59)	Agricultural	23.0	8.0	67.0	19.5	6.0	45.0	51.7	20.4	106.9	105.1	41.4	217.0	0.1	0.0	1.3
	Living	45.0	17.0	73.0	8.5	3.0	14.0	30.6	14.4	46.8	62.2	29.2	95.1	0.0	0.0	0.0
	Drinking	19.0	4.0	74.0	11.6	3.0	51.0	38.5	13.2	129.7	78.2	26.8	263.4	0.0	0.0	0.0
	Ave.	22.0	4.0	74.0	14.4	3.0	51.0	43.2	13.2	129.7	87.6	26.8	263.4	0.0	0.0	1.3
Oct. (n=11)	Agricultural	16.0	8.0	22.0	17.6	4.9	34.0	53.5	34.8	76.8	108.7	70.7	156.0	0.0	0.0	0.0
	Living	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Drinking	22.0	4.0	49.0	12.9	0.0	34.0	45.7	11.4	127.9	92.8	23.2	259.7	0.0	0.0	0.0
	Ave.	20.0	4.0	49.0	14.7	0.0	34.0	48.5	11.4	127.9	98.5	23.2	259.7	0.0	0.0	0.0
Nov. (n=10)	Agricultural	23.0	7.0	47.0	20.3	6.0	30.0	65.8	36.6	129.6	133.5	74.4	263.3	0.1	0.0	0.4
	Living	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Drinking	17.0	4.0	34.0	10.0	3.0	18.0	24.1	8.4	63.1	49.0	17.1	128.1	0.0	0.0	0.0
	Ave.	19.0	4.0	47.0	14.1	3.0	30.0	40.8	8.4	129.6	82.8	17.1	263.3	0.0	0.0	0.4
Usage (n=145)	Agricultural	29.0	6.0	167.0	20.1	1.6	60.8	53.6	18.0	140.4	108.9	36.6	285.2	0.1	0.0	1.3
	Living	39.0	17.0	73.0	21.4	3.0	34.5	47.7	14.4	82.6	96.8	29.2	167.8	0.0	0.0	0.0
	Drinking	23.0	4.0	74.0	12.8	0.0	51.0	37.2	8.4	131.4	75.5	17.1	266.9	0.0	0.0	0.1
	Ave.	27.0	4.0	167.0	16.7	0.0	60.8	45.7	8.4	140.4	92.7	17.1	285.2	0.0	0.0	1.3
Seasonal (n=145)	Pre-monsoon	32.0	5.0	160.0	19.4	0.0	57.2	48.6	15.6	140.4	98.6	31.7	285.2	0.0	0.0	0.4
	Post-monsoon	25.4	4.0	167.0	16.0	0.0	60.8	45.1	10.8	139.0	91.5	21.9	282.3	0.0	0.0	1.3

pre-monsoon period, so we inferred that many pollutants from surface water sources affected the groundwater quality of samples from the post-monsoon season. Chloride is present in all natural waters, but usually in relatively small amount, and is considered a strong acid compared to other ions. The chloride concentration ranged from 27.0 to 167.0 mg/L on average, with the maximum concentration found in the July samples of the agricultural area. Sulfate is widely distributed in reduced form in both metamorphic and sedimentary rock as a metallic sulfide, but it is not a major constituent of the Earth's outer crust. The sulfate concentration in the groundwater samples ranged from 0.0 to 60.8 mg/L. It is well known that sulfate concentration in natural water is less than that of chloride, which was observed in the groundwater of this study. Thus, it could be supposed that the sulfate concentration of the groundwater might be influenced by agricultural patterns, as synthetic chemical fertilizers and manure were used in the farm fields and rice paddies. The primary source of carbonate and bicarbonate ions in groundwater is the dissolved carbon dioxide in rainwater. Bicarbonate combines with calcium carbonate and sulfate to form heat retarding. Pipe-clogging scale in boilers and in other heat exchange equipment. Bicarbonate values ranged from 17.1 to 285.2 mg/L, making it the dominant anion of the study area. It is known that higher concentrations of bicarbonate might be influenced by the weathering of silicate rocks and the infiltration of rainwater through the soil layers. The concentration of carbonates ranged from 8.4 to 140.4 mg/L, with the maximum concentrations observed in the agricultural samples.

3.3. Evaluation of groundwater for agricultural use

3.3.1. SAR, Na (%), RSC, PI, SSP, MH, KR, and PI

As mentioned in the Introduction, the main purposes of this study were the classification of groundwater for agricultural usages and the assessment

of groundwater quality by using the interrelationships among the evaluation equations. The suitability of groundwater for irrigation is contingent on the effects of the mineral constituents in the water on both the plants and soil. Generally, salts can harm a plant's growth physically by limiting the uptake of water through modification of the osmotic processes or chemically via metabolic reactions, such as those caused by toxic constituents. Salts in soils cause changes in soil structure, permeability, and aeration, which indirectly affect plant growth. An important factor in the relation of crop growth to water quality is drainage. If a soil is open and well-drained, crops may be grown in it with the application of generous amounts of saline water; on the other hand, a poorly drained area combined with application of good quality water may fail to produce as satisfactory a crop. Therefore, many hydrochemical parameters of groundwater, such as EC, sodium (%), SAR, RSC, PI, and MR, are used for determining its suitability for irrigation. From applying the equations and classifications for evaluating groundwater (Table 2), we obtained the following classifications: SAR [Excellent (100%), Na (%) [Excellent (2.1%), Good (51.7%), Permissible (39.3%), Doubtful (6.2%), Unsuitable (0.7%)], RSC [Good (100%)], PI [Excellent (100%)], SSP [(Excellent (0.7%), Good (37.2%), Fair (61.4%), Poor (0.7%)], MH [Acceptable (96.6%), Non-Acceptable (3.4%)], KR [Permissible (30.3%), Non-Permissible (69.7%)], and PS [Excellent to Good (100%)], the results of which are shown in Tables 6 and 7.

3.3.2. Evaluation of groundwater using Wilcox and U.S. Salinity Laboratory diagrams

EC and Na concentrations are important in classifying irrigation water because high saline content (high EC) in irrigation water leads to formation of saline soil. The salinization of rice paddies is the major cause of production loss and it has an adverse effect on irrigation systems, including groundwater quality of stream and lake water because irrigation water on rice paddies drains to streams

Table 6. Classifications of groundwater using SAR, Na (%), RSC, and PI

Classifications	SAR				Na (%)					RSC		PI			
	10–20	Excellent (E)			Up to 20		Excellent (E)			< 1.25	Good/Safe (G)	> 75%	Excellent (E)		
Grade Usage	10–18	Good (G)			20–40		Good (G)			1.25–2.5	Medium/Marginal (M)	25–75%	Good (G)		
	18–26	Fair (F)			40–60		Permissible (P)			> 2.5	Bad/Unsuitable (B)	> 25%	Unsuitable (U)		
Grade Usage	> 26	Poor (P)			60–80		Doubtful (D)			-	-	-	-		
	-	-			> 80		Unsuitable (U)			-	-	-	-		
Grade Usage	(E)	(G)	(F)	(P)	(E)	(G)	(P)	(D)	(U)	(G)	(M)	(B)	(E)	(G)	(U)
Agriculture	49.0	0.0	0.0	0.0	0.7	24.8	21.4	1.4	0.7	49.0	0.0	0.0	49.0	0.0	0.0
Living	4.1	0.0	0.0	0.0	0.0	3.4	0.7	0.0	0.0	4.1	0.0	0.0	4.1	0.0	0.0
Drinking	46.9	0.0	0.0	0.0	1.4	23.4	17.2	4.8	0.0	46.9	0.0	0.0	46.9	0.0	0.0
Total (%)	100.0	0.0	0.0	0.0	2.1	51.7	39.3	6.2	0.7	100.0	0.0	0.0	100.0	0.0	0.0
	145 (100%)				145 (100%)					145 (100%)		145 (100%)			

Table 7. Classifications of groundwater using SSP, MH, KR, and PS

Classifications	SSP				MH		KR		PS			
	< 20	Excellent (E)			> 50	Non-Acceptable (NA)	> 1.0	Non-Permissible (NP)	< 5	Excellent to Good (E)		
Grade Usage	20–40	Good (G)			< 50	Acceptable (A)	< 1.0	Permissible (P)	5–10	Good to Injurious (G)		
	40–80	Fair (F)			-	-	-	-	> 10	Injurious to Unsatisfactory (I)		
Grade Usage	> 80	Poor (P)			-	-	-	-	-	-		
	(E)	(G)	(F)	(P)	(NA)	(A)	(NP)	(P)	(E)	(G)	(I)	
Agriculture	0.0	18.6	29.7	0.7	2.8	46.2	15.9	33.1	49.0	0.0	0.0	
Living	0.0	2.8	1.4	0.0	0.0	4.1	0.0	4.1	4.1	0.0	0.0	
Drinking	0.7	15.9	30.3	0.0	0.7	46.2	14.5	32.4	46.9	0.0	0.0	
Total (%)	0.7	37.2	61.4	0.7	3.4	96.6	30.3	69.7	100.0	0.0	0.0	
	145 (100%)				145 (100%)		145 (100%)		145 (100%)			

or lakes for the circulation of rice paddy water. Thus, the introduction of saline water from the ground to the rice paddy should be monitored regularly. Judgement through multi-criteria such as conductivity and SAR would be a proper tool for maintaining high productivity of rice paddies because saline conditions severely limit the choice of crops and adversely affect crop germination and yields. In this respect, it is important that all evaluations regarding irrigation water quality be linked to the evaluation of the soils to be irrigated. Most of all, sodium concentration is important in classifying irrigation water because sodium reacts with soil, reducing its permeability. In all natural waters, perc-

ent sodium is a parameter with which to evaluate its suitability for agricultural purposes, as sodium combining with carbonate forms alkaline soils and sodium combining with chloride forms saline soils. Either type of sodium-enriched soil will lead to little or no plant growth. In addition to that mentioned in section 3.3.1, another method for determining groundwater samples was studied by plotting analytical data relating EC to sodium percent (Fig. 1(a)), which showed that most of the samples were “Excellent to good.” Based on EC values, Richards classified the total concentration of soluble salts in irrigation water into four groups. High-salinity problems are encountered when irrigation acti-

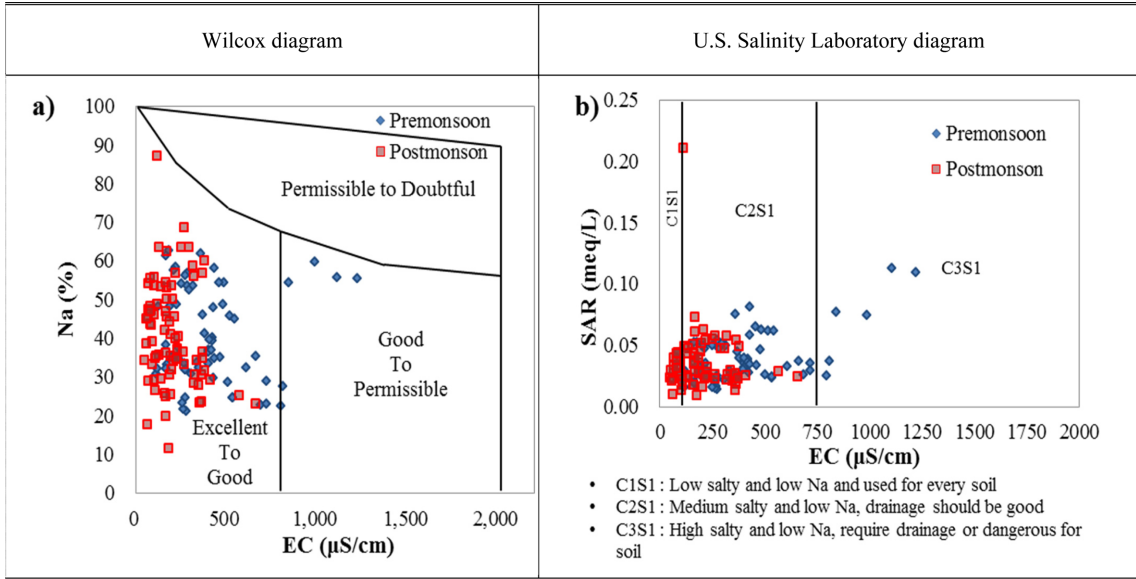


Fig. 1. Wilcox diagram (a) and U.S. Salinity Laboratory diagram (b) of the studied groundwater.

vity is in agricultural soils with poor drainage and when water logging allows the water table to rise close to the root zone of plants, causing accumulation of sodium salts in the soil solution through

capillary action following surface evaporation. The sodium or alkali hazard in the use of water for irrigation is determined by the absolute and relative concentrations of cations. The relative activity of

Table 8. Classification of groundwater quality based on SAR and conductivity per USSL classifications (after Ayers and Westcot, 1985³³; U.S. Salinity Laboratory, 1954³⁴; Wilcox, 1955¹²)

Wilcox diagram		Classifications and ranges		
		Classification	Range	Quality
	Conductivity	C1	100-200	Excellent
		C2	250-750	Good
		C3	750-2250	Doubtful
		C4-C5	> 2250	Unsuitable
	SAR	S1	< 10	Excellent
		S2	10-18	Good
		S3	19-26	Doubtful/Fairly
		S4-S5	> 26	Unsuitable

sodium ion in the exchange reaction with soil is expressed in terms of SAR. If high sodium content and low calcium content are present in waters used for irrigation purposes, the base-exchange complex may become saturated with sodium. This can destroy the soil structure because of deflocculation (dispersion of clay particles) processes. The U.S. Salinity Laboratory diagram uses electrical conductivity, and SAR classifies groundwater as C_xS_x , which is a combination of electrical conductivity (C1-C4) and SAR (S1-S4) (Table 8). The plotting of the analytical data on the US Salinity Laboratory diagram, in which the EC is taken as a salinity hazard

and SAR as an alkalinity hazard (Fig. 1(b)), shows that most pre-monsoon and post-monsoon samples were classified as C1S1 (Excellent/Excellent) and C2S1 (Good/Excellent).

3.4. Piper diagram

Water types of the Piper diagram (Fig. 2) were classified into the following groups: 1) water groups high in both $Ca^{2+}+Mg^{2+}$ and $Cl^{-}+SO_4^{2-}$, which results in an area of permanent hardness; 2) water groups rich in $Ca^{2+}+Mg^{2+}$ and HCO_3^{-} , which indicates a region of water with temporary hardness; 3) water groups primarily composed of alkali car-

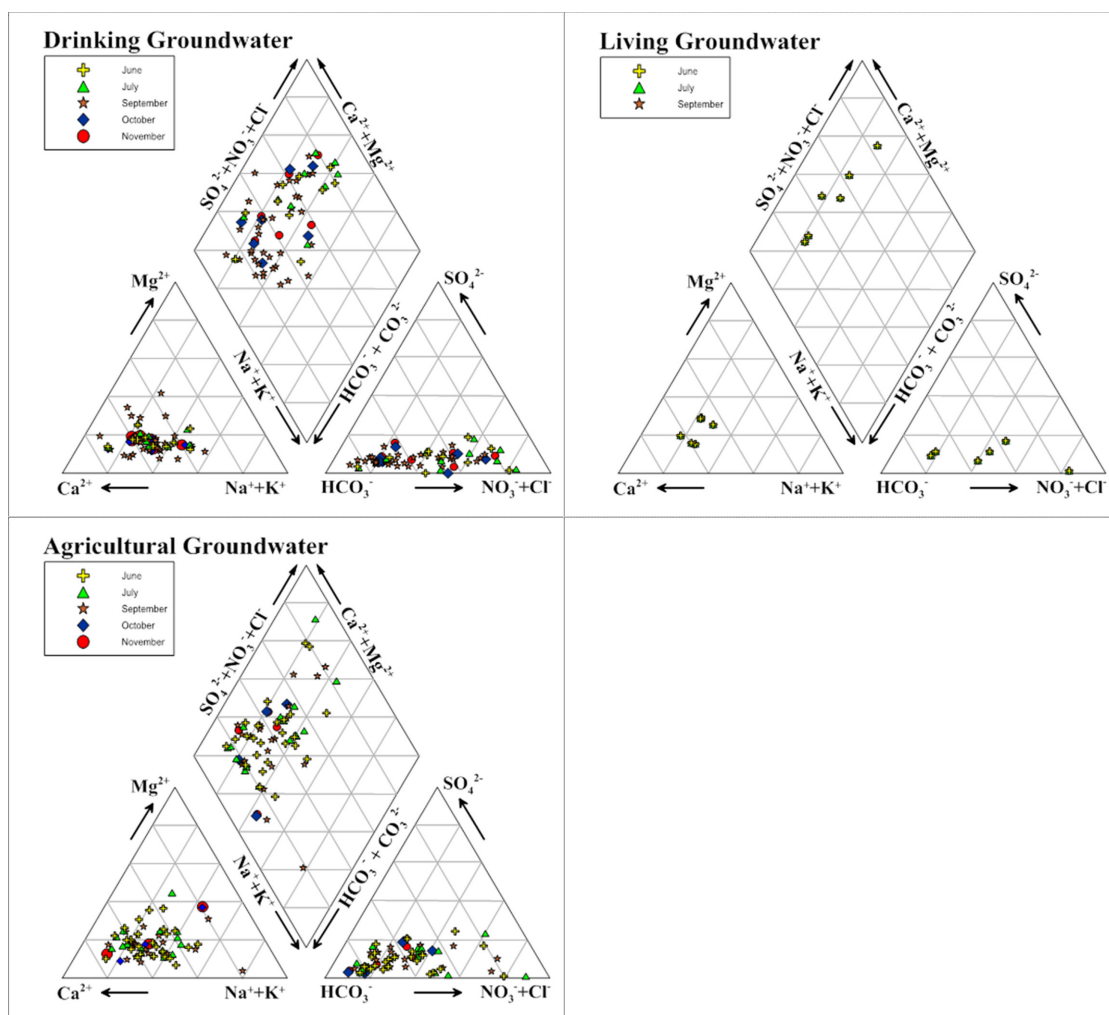


Fig. 2. Piper diagram of the studied groundwater per usage purpose.

bonates ($\text{Na}^+ + \text{K}^+$ and $\text{HCO}_3^- + \text{CO}_3^{2-}$); and 4) water groups considered saline ($\text{Na}^+ + \text{K}^+$ and $\text{Cl}^- + \text{SO}_4^{2-}$). The dominant types of groundwater are regarded as a key factor for the conjecture of the contamination sources from the upper layers of soils and surface waters including water from streams, reservoirs, lakes, and the sea. Moreover, it would be regarded as a major signal for presuming the main source from chemical fertilizers and manure induced by agricultural activities and by other productive activities on farm fields. As mentioned in the Introduction, water types from the Piper diagram are regarded as major key factors

for linking inorganic sources of groundwater to soil texture, so they could be linked to the Gibb and Chadha diagrams in section 3.5. For the classifications of the groundwater, samples were classified for their usages such as drinking, living, or industrial use (Fig. 2) and also divided per their sampling period: pre-monsoon (June) and post-monsoon (July, September, October) (Fig. 3). The major types of groundwater samples were divided into $\text{Ca}^{2+} - (\text{Cl}^- - \text{NO}_3^-)$ and $\text{Ca}^{2+} - \text{HCO}_3^-$ types, so it would be known if there was influence from inorganic sources in the soil upper layers and chemical fertilizers. However, there were no specific differences of

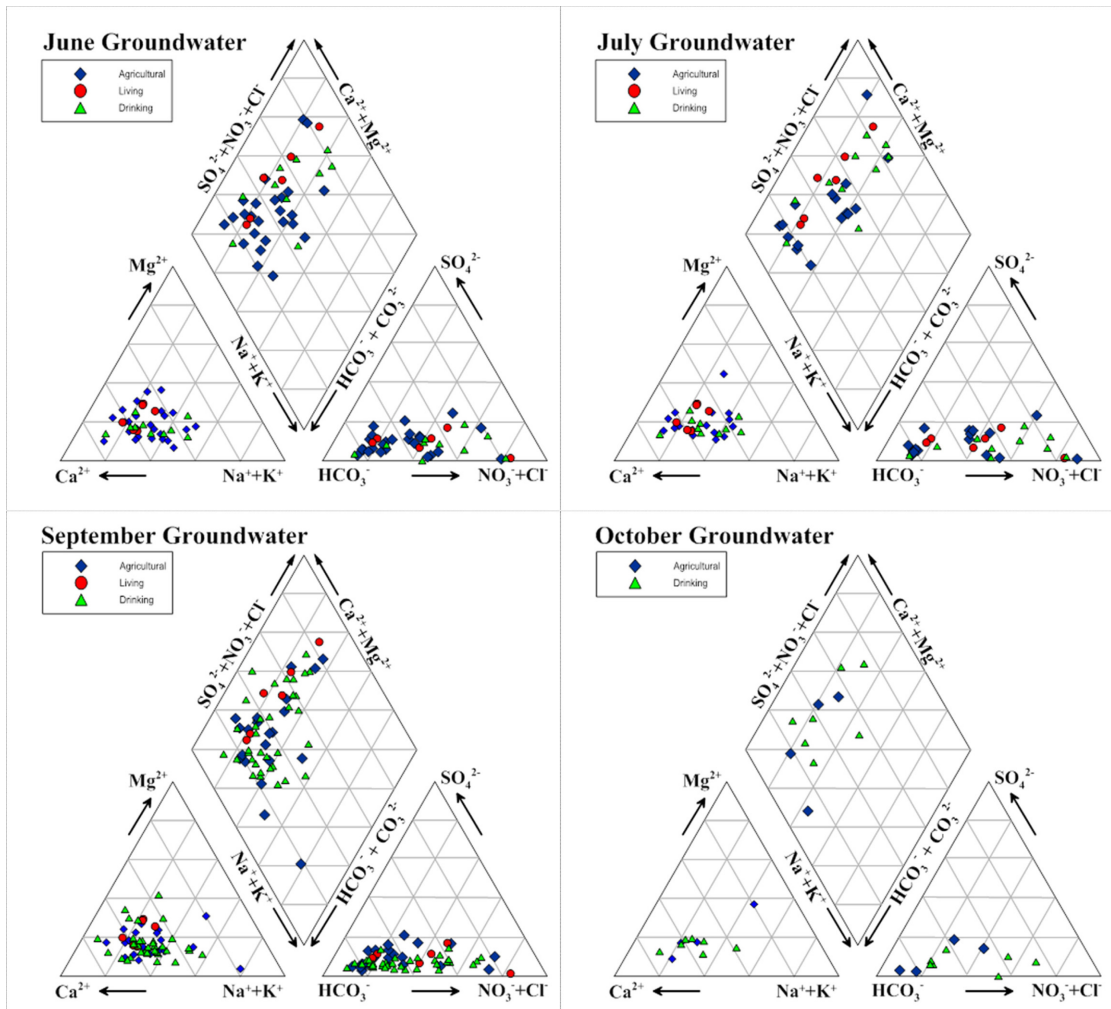


Fig. 3. Piper diagram of the studied groundwater per seasonal variation, from June to October.

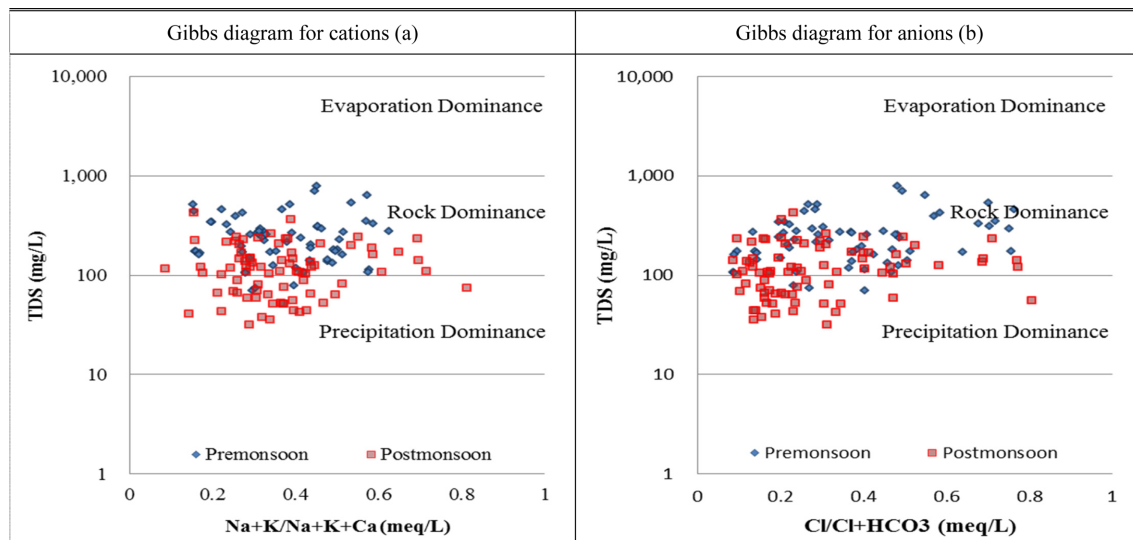


Fig. 4. Gibbs diagrams of the studied groundwater for cations (a) and anions (b).

water types of the groundwater between usage groups nor sampling period groups.

3.5. Estimation of origin of ions using the Gibbs and Chadha diagrams

Whereas the Piper diagram classifies groundwater based on the distribution of both cations and ani-

ons, the Gibbs diagram estimates the origin of ions in groundwater by focusing on the correlation between the concentration of cations (Na^+ , Ca^{2+}), anions (Cl^- , HCO_3^-), and TDS. The Gibbs diagrams based on TDS and the concentration of cations (Fig. 4(a)) and anions (Fig. 4(b)) show that most of the cations and anions in groundwater have a rock-

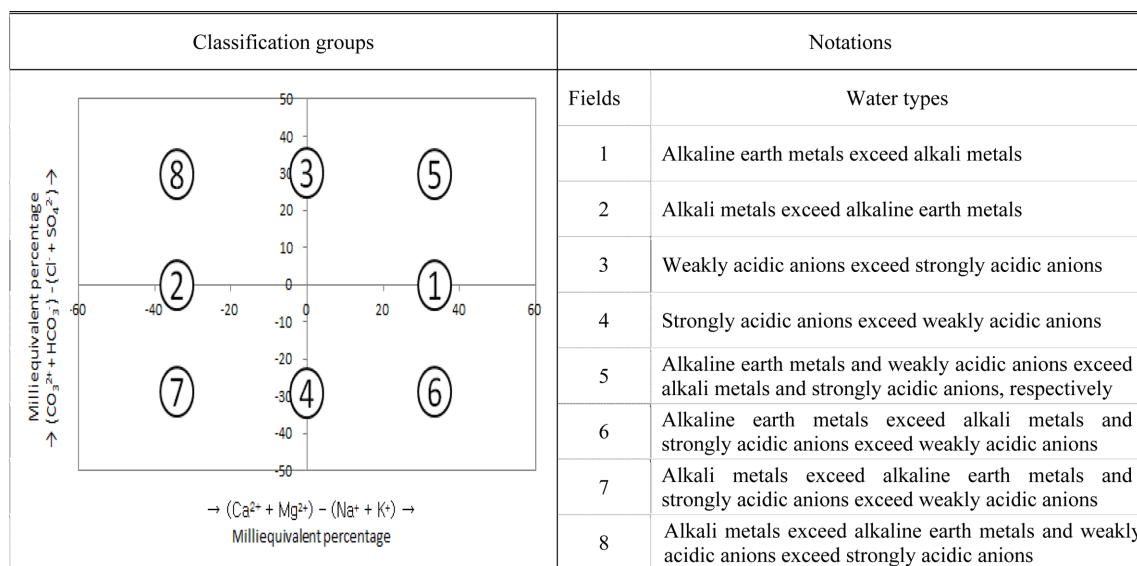


Fig. 5. Geochemical classifications and hydrochemical parameters of the studied groundwater (D. K. Chadha, 1999).

dominance origin. This characteristic indicates that the dissolution of ions in groundwater through the interaction between groundwater and rock or soil is more dominant than that of precipitation or any other sources. Chadha proposed a modified diagram and classified the origin of ions into eight groups. In a Chadha diagram, the square or rectangular field describes the overall ion distribution and character of groundwater for the demonstration of geochemical classification and hydrochemical processes of groundwater. To define the primary character of groundwater, the rectangular field is divided into eight subfields, each of which represents a water type (Fig. 5). The tracing study of ions based on the Chadha diagram indicated that the alkaline earth and alkali metals that originate from soil or rock interactions with weak acidic anions and strong acidic anions in groundwater interacted (Fig. 6). In the Gibbs and Chadha diagrams, it was supposed that the dominance type of the groundwater could be concluded in the Gibbs diagram (hydrochemical) and the dominance type of components in a specific range would be defined in the Chadha diagram (geochemical), hence the combination of the two diagrams would be a convenient tool for illustrating

the general types of groundwater at laboratory scale.

4. Conclusion

The major goals of this study were classified into four categories: on-site monitoring of groundwater quality via instrumental and laboratory experiments; assessment of groundwater quality for agricultural usages via SAR, Na (%), RSC, PI, SSP, MH, PS, and KR; classification of groundwater by using Piper, Gibbs, and Chadha diagram methods; and tracking of the origins of anions and cations by using rock-dominance types. In the monitoring of ionic properties of groundwater, it was concluded that the concentrations of cations, such as Ca^{2+} , Na^+ , K^+ , and Mg^{2+} , and anions, such as HCO_3^- , and Cl^- , were higher in the post-monsoon season than in the pre-monsoon season, indicating groundwater quality might be influenced by chemical fertilizers and manure introduced through agricultural activities. For the assessment of the groundwater quality, the SAR, Na (%), RSC, PI, SSP, MH, PS, and KR were calculated by using equations for each and the results were classified as follows: 100% excellent for SAR, 51.1% good for Na (%), 100%

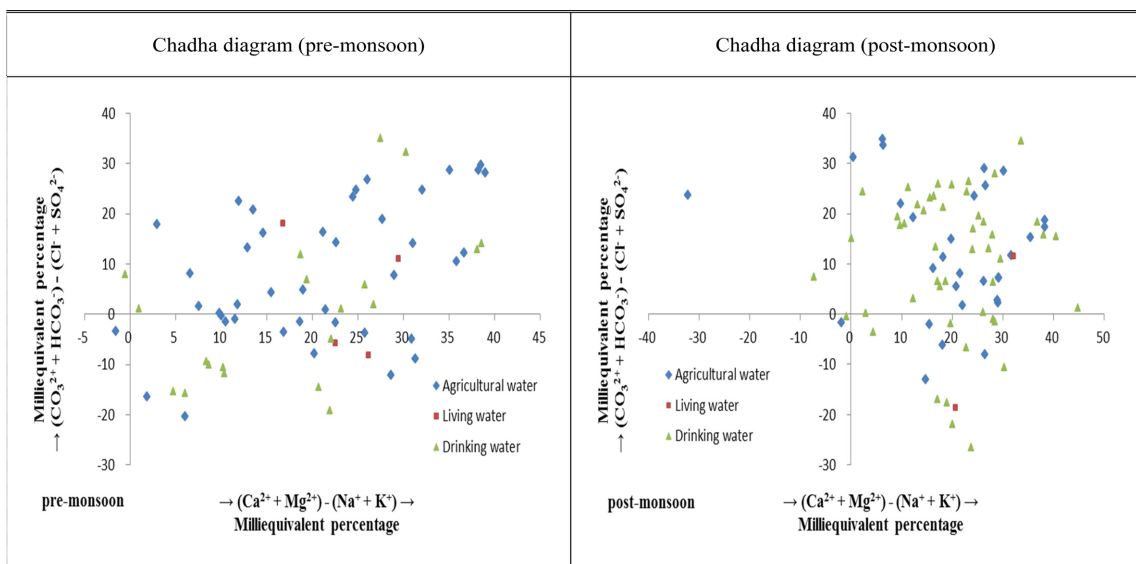


Fig. 6. Seasonal geochemical classifications and hydrochemical parameters of the studied groundwater.

good for RSC, 100% excellent for PI, 61.4% fair for SSP, 96.6% acceptable for MH, and 69.7% permissible for KR. Most of the groundwater samples were classified as “excellent to good” or “good to permissible” using the Wilcox diagram. The evaluation using the U.S. Salinity Laboratory diagram also showed that most groundwater samples were grouped as C1S1 (Excellent/Excellent) or C2S1 (Good/Excellent). In the Piper diagrams, the Ca^{2+} –(Cl^- – NO_3^-) and Ca^{2+} – HCO_3^- types, which are known as the general type of groundwater in rural areas of Korea, were the dominant types for the study’s groundwater. Moreover, in source-rock deduction in accordance with the Gibbs and Chadha diagrams, the chemical components in the groundwater were affected by the water-rock interactions as follows: dolomite type weathering, gypsum type weathering, and alkali and alkaline earth metal type weathering.

References

1. M. Vasanthavigar, K. Srinivasamoorthy, R. R. Ganthi, K. Vijayaragavan, and V. S. Saram, “Characterization and quality assessment of groundwater with a special emphasis on irrigation utility: Thirumanimuttar sub-basin, Tamil Nadu”, India, *Arab. J. Geosci.*, **2012**, 5, 245-258.
2. M. J. A. Abdul Hameed, A. A. S. Mukheled, J. K. Abass, A. M. Athmar, “Evaluation of treated municipal wastewater quality for irrigation”, *Journal of Environmental Protection*, **2010**, 1, 216-225.
3. S.R. Barick and B. K. Ratha, “Hydro-chemical analysis and evaluation of groundwater quality of hial area”, Bolangir District, Odisha, India, *Journal of Geosciences and Geomatics*, **2014**, 2, 22-28.
4. S. Shubhra, N. J. Ruju, and C. H. Ramakrishna, “Evaluation of groundwater quality and its suitability for domestic and irrigation use in parts of the chandauli-vernashi region”, Uttar Pradesh, India, *Journal of Water Resource and Protection*, **2015**, 7, 572-587.
5. E. A. Kaka, T. T. Akiti, V. K. Nartey, E. K. P. Bam, and D. Adomako, “Hydrochemistry and evaluation of groundwater stability for irrigation and drinking purpose in the southeastern Volta river basin: Many korobo area”, Ghana, *Elixia Agriculture*, **2011**, 39, 4973-4807.
6. B. Chakraborty, K. Adhikari, K. Sadhu, and A. Gopadhyay, “Hydrochemistry of aquifers as a function of underground mining of gondwana coal: Eastern fringe of raniganj coalfield”, India, *International Journal of Research in Chemistry and Environment*, **2012**, 2, 310-322.
7. A. Yinusa, A. Bello, O. O. Franklin, A. Omolara, Duvbiana, O. I. Jeremiah, A. Adeyemi, and T. O. Miriam, “Hydrochemical evaluation of groundwater in akura area”, Southwestern Nigeria, for Irrigation Purpose, *European International Journal of Science and Technology*, **2013**, 2.
8. B. S. Badmus, V. C. Ozebo, O. A. Idowu, S. A. Ganiyu, and O. T. Olurin, “Groundwater assessment of hand dug wells around open landfill in Ibadan metropolis for domestic and irrigation purpose”, *Journal of Water Resource and Protection*, **2014**, 6, 1412-1424.
9. S. Radhey and G. S. Kalwania, “Groundwater chemistry: A case study of eastern part of Sikar city (Rajasthan), India”, *International Journal of Applied Engineering Research*, *DINDIGUL*, **2011**, 2.
10. I. Gabriel, Obienfuna, M. Donatus, and Orazulike, “The hydrochemical characteristics and evolution of groundwater in semiarid Yola area”, Northeast, Nigeria, *Research Journal of Environmental and Earth Sciences*, **2011**, 3, 400-416.
11. J. M. Ishaku, A. S. Ahmed, and M. A. Abubakar, “Assessment of groundwater quality using chemical indices and GIS mapping in Jada area, Northeastern Nigeria”, *Journal of Earth Sciences and Geochemical Engineering*, **2011**, 1, 35-60.
12. L. V. Wilcox, “Classification and use of irrigation water”, **1955**, USDA, Washington (Circular 969).
13. L. A. Richards, “Diagnosis and improvement of saline and alkali soils. Hand Book”, **1954**, No. 60. U.S. Department of Agriculture, Washington, D.C.
14. A. M. Piper, “A graphic procedure in geochemical interpretation of water analysis”. *U.S. Geol. Surv., Groundwater Note*, **1953**, 12, 63.
15. R. J. Gibbs, “Mechanism controlling world water chemistry”, *Science*, **1970**, 170, 3962, 1088-1090.
16. D. K. Chadha, “A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data”, *Hydrogeology Journal*, **1999**, 7, 431-439.
17. B. R. Scanlon, “Physical controls on hydrochemical variability in the inner bluegrass Karst region of Central Kentucky”, *Ground Water*, **1989**, 27, 5.
18. K. Srinivasamoorthy, M. Gopinath, S. Chidambaram, M. Vasanthavigar, and V. S. Saram, “Hydrochemical characterization and quality appraisal of groundwater

- from Pungar sub basin, Tamilnadu, India”, *Journal of King Saud University - Science*, **2014**, 26, 37-52.
19. N. Subba Rao, “Seasonal variation of groundwater quality in a part of Guntur district, Andhra Pradesh”, *India Environmental Geology*, **2002**, 49, 413-429.
 20. N. Agahazadeh and A. A. Mogddam, “Assessment of groundwater quality and its stability for drinking and agricultural uses in the Oshnavieh area, northwest of Iran”, *Journal of Environmental Protection*, **2011**, 1, 30-40.
 21. J. R. Nandimandalam, U. K. Shukla, and P. Ram, “Hydrogeochemical for the assessment of groundwater quality in Varanasi: a fast-urbanizing center in Uttar Pradesh, India”, *Environ Monit Assess*, **2011**, 173, 279-300.
 22. S. K. kumar, A. Logeshkumaran, N. S. Magesh, P. S. Godson, N. Chandrasekar, “Hydro-geochemistry and application of water quality index (WQI) for groundwater quality assessment, Anna Nager, part of Chennai City, Tamil Nadu, India”, *Appl. Water Sci.*, **2015**, 5, 335-343.
 23. E. Lakshmanan, R. Kannan, and M. S. Kumar, “Major ion chemistry and identification of hydrochemical processes of groundwater in a part of Kancheepuram district, Tamil nadu”, *India. Environ. Geosci.*, **2003**, 10, 156-166.
 24. Ministry of Environment, “Official testing method with respect to water pollution process”, **2013**, Korea.
 25. L. A. Richards, “Diagnosis and Improvement of Saline Alkali Soil”, *Agricultural Handbook*, **1954**, 60, USDA, Washington, D.C.
 26. L. D. Doneen, “Notes on water quality in agriculture”, **1964**, Published as a Water Science and Engineering, Paper 4001, Department of Water Sciences and Engineering, University of California.
 27. D. M. Joshi, A. Kumar, and N. Agrawal, “Assessment of the irrigation water quality of River Ganga in Haridwar district India”, *J. Chem.*, **2009**, 2, 285-292.
 28. K. V. Paliwal, “Irrigation with saline water”, **1972**, Monogram no. 2 (New series). New Delhi, IARI, 198.
 29. W. P. Kelly, “Use of saline irrigation water”, *Soil Sci.*, **1963**, 95, 353-391.
 30. L. D. Doneen, “Salination of soil by salts in the irrigation water”, *American Geophysical Union Transactions*, **1954**, 35, 943-950.
 31. M. H. Ei-Sayed, Moustafa, M. A. El-Fadi, and H. A. shawky, “Impact of hydrochemical process on groundwater quality, Wadi Feiran, South Sinai”, *Australian Journal of Basic and Applied Sciences*, **2012**, 6, 638-654.
 32. D. R. Champ, J. Gulenes, and R. E. Jackson, “Oxidation-reduction sequences in ground-water systems”, *Canadian Journal of Earth Sciences*, **1979**, 16, 1466-1472.
 33. R. S. Ayers and D. W. Westcot, “Water quality for agriculture FAO irrigation drain”, **1985**, 29, 1-109.
 34. U. S. Salinity Laboratory, “Diagnosis and improvement of saline and alkaline soils”, U. S. Dept. of Agriculture. Hand book, **1954**, 60, 160.