

Applications of Hydrochemical Models for Groundwater in Korea

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Abstract

The variation patterns of groundwater mobility and chemical distribution are regarded as a very important factor for determining the geochemical features and therefore, the classifications of groundwater based on the chemical properties are highly valued for the expansion of study areas for setting up the regulations and management plans of governmental level for the preservation of local groundwater. Based on these prerequisites, in this study we focused on the evaluations, the comparison of the physiochemical characteristics and distribution of cations and anions in groundwater samples sampled in rural areas of Korea. The major goals of this study were classified as four categories such as followings; 1. On-site monitoring of groundwater qualities by instrumental and laboratory experiment, 2. Classifications of groundwater by using of Piper, Gibbs and Chadah diagram methods, 3. Tracking of the origins of anions and cations by using of rock-dominance types and relative ionic distributions. As a result of this study, the classifications of groundwater based on the Piper diagram showed that the groundwater type is grouped as the Ca^{2+} -(Cl^- - NO_3^-) and Ca^{2+} - HCO_3^- type groups and these types are known as the general features of groundwater in Korea. And the tracking of dominance types (classified as evaporation, rock, precipitation) based on the Gibbs diagram have shown that the origins of anions and cations in groundwater are the rock-dominance. In the applications of CAI 1 and CA 2, the negative values were more dominance than positive values so there might be reverse ion reaction between groundwater and rock-soils. Finally, by the carbonate weathering, silicate weathering and evaporation diagrams there were more complex mechanisms in chemical evolutions induced by the lithological influences such as weathering processes, ion exchange and other anthropogenic sources.

Keywords: Groundwater, Piper diagram, Gibbs diagram, Wilcox diagram, US salinity Laboratory's Diagram, Chadah diagram

1. Introduction

Groundwater contains a wide range of dissolved solids and contain small amount of dissolved organic matter and gases. Groundwater, which is always in motion through aquifers and it interacts with the aquifer material in the subsurface environment. During this movement groundwater may dissolve, transport and deposit mineral matter. These changes are mainly based on the surface and subsurface environment. The ionic composition of groundwater is controlled by the chemical composition of rain, composition of infiltrating surface water, properties of soil and rock in which the groundwater moves, contact time and contact surface between groundwater and geological material along its flow path, rate of geochemical (oxidation/reduction ion exchange, dissolution, evaporation, precipitation) process and microbiological process. So, the understanding of geochemical processes help to get an insight into the contributions of rock-water interaction that influences groundwater quality and these geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry (Kumar *et al.*, 2006). Groundwater chemically evolves by interacting with aquifer minerals or internal mixing among different groundwater along flow-paths in the subsurface. Therefore, it has been known that the increase of the ionic concentrations in the groundwater is caused by spatially variable recharge and governed by geochemical evolution controls. Furthermore, the weathering of primary and secondary minerals from the rocks and soil are also contributing cations and silica in the system (Jacks, 1973; Freeze and Cherry, 1979). Geologists have made an effort to set up the analytical method and to establish the mechanisms of natural circulation processes such as leaching and dissolution, mixing, cation exchange, oxidation-reduction, precipitation, hydrolysis control the water quality during its movement from the recharge to

discharge areas. And, evaluation of these changes of groundwater surely help to simplify and organize data set in order to make useful generalizations and insight. As mentioned, we tried to classify the groundwater samples in pre-monsoon and post-monsoon periods from rural areas of Korea using various modelling methods and tried to infer inorganic source of groundwater through Piper (1953) diagram, Gibbs (1970) diagram and Chadah (1999) diagram. On the chemistry of groundwater it was attempted to know that the hydrochemical processes that mostly influence the species of groundwater chemistry are reaching and dissolution of weathered rocks of subsoil region with some influence of revers and ion exchange water-rock interaction, or not.

2. Method

2.1 Sampling 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, the representative samples from the sampling sites or wells may have the meaning of different things to different investigations, due mainly to 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 acknowledge 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 of groundwater sampling and in situ measurement for on site items. In this study, all samples were collected for two different seasons representing (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 bottle acid washed, well rinsed low density polyethylene bottles with inside stopper from bore wells and analyzed for chemical parameters guidelines. The samples were collected after pumping the wells for enough time of 15~20 min and subsequent filtering through 0.45 μm membranes was done. The analyzed parameters include the activity of hydrogen ion concentration (pH), electrical conductivity (EC), total hardness (TH), total dissolved solids (TDS) and cation groups like Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}) and anion groups like bicarbonate (HCO_3^{-}), Chloride (Cl^{-}), Nitrate (NO_3^{-}), Phosphate (PO_4^{3-}). The pH and electrical conductivity (EC) were measured using pH and EC meters. All anions and cations were analyzed by Ion chromatography (Dionex) and analytical conditions of anion and cation for groundwater were shown in Table. 1. Following the guidelines, quality controls and quality assurances were undertaken by checking every steps for the guarantee of miscellaneous factors such as followings; calibration curves, blanks, sample preservations, duplicate samples, standards, and charge balances of ionic substances

2.2 Chemical Analysis

The selection of analytical method is determined by 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 the DX-500 Ion Chromatography from Dionx, and Ionpac A CS12A column was used to analyze the cations while an Ionpac AS12A column was used for the analysis of the anions. The Standard Chemical Analysis Guidelines for Water and Wastes were used as the test standard for industrial water while the Standard Chemical Analysis Guidelines for Water was used for drinking water samples. Tests were carried out repeatedly to satisfy the value presented by the standard test method in order to verify the precision and accuracy of the analysis, and the analysis conditions for cations and anions using ion chromatography is shown below in Table. 1. The alkali components hydroxides (OH^{-}), carbonates (CO_3^{2-}) and bicarbonates (HCO_3^{-}) were converted to a calcium carbonate (CaCO_3) concentration to represent the alkalinity, and the Standard Method (AWWA, 1997) was used as the test method. The phosphate was measured using the test method for phosphates described in the Standard Method, which is based on the optical absorbance of the 880nm wavelength caused by a mixture of an ammonium molybdate solution and an ascorbic acid solution.

Table 1. Analytical conditions of anion and cation for groundwater

Items	Anion	Cation
Couluumn	IonPac AS12A, 4 mm x 250 mm	IonPac CS12A, 4 mm x 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 uL	50 uL
Detector	Electric conductivity detector	Electric conductivity detector

2.3 Classifications of Groundwater Types from Graphical Models

2.3.1 Piper Model

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

2.3.2 Gibbs Model

Gibbs diagram is used to interpret the effect of hydrogeochemical processes such as precipitation, rock-water interaction mechanism 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. Gibbs ratio is calculated using the following equation (1) and (2);

$$\text{Gibbs ratio I (for anion)} = (\text{Cl}^-) / (\text{Cl}^- + \text{HCO}_3^-) \quad (1)$$

$$\text{Gibbs ratio II (for cation)} = (\text{Na}^+ + \text{K}^+) / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}) \quad (2)$$

2.3.3 Chloro Alkaline Index (CAI 1, CAI 2) Model

The ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the chloro-alkaline indices. To know the direction of exchange during the path of groundwater through the aquifer, Schoeller (1965) suggested 2 chloroalkaline indices CAI1 and CAI2 to indicate the exchange of ions between groundwater and its host environment. The ion exchange and reverse ion exchange were confirmed by using chloro-alkaline indices following the equation (3) and (4);

$$\text{CAI 1} = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / \text{Cl}^- \quad (3)$$

$$\text{CAI 2} = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / \text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^- \quad (4)$$

2.3.4 Chadah Model

Chadah diagram is a somewhat modified version of the Piper diagram and the expanded Durov (1948) diagram. The difference in milliequivalent percentage between alkaline earths (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 sulphate) is plotted on the Y axis. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would plot in one of the four possible sub-fields of the proposed diagram.

2.3.5 Mechanisms of Chemical Process

Groundwater derives its mineral character essentially from reactions between rain water and the host rock over a time scale of days, months or years during percolation. The extent of this water-rock interaction is controlled by the residence time of the water and the mineralogy of the aquifer matrix. Alteration of water chemistry in groundwater can occur through physical, chemical and biological processes. In this respects, the hydrochemical process occurring within groundwater zone by interactions within minerals dissolved in aquifer resulted in the chemical nature of groundwater. And the geochemical processes are regarded as very important factors because they control the compositions and distributions of anion and cation in the aquifer. And also, the geochemical properties of groundwater bodies are determined by the chemistry and its correlations between anion and cation.

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 and this is be kept well 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 most common physical parameters were measured in the field at the time of sampling are pH, EC, DO, Eh and these parameters provide a useful and preliminary information of the area. And for the comparison of on-site factors by the usages and variations patterns of sampling periods, groundwater samples were classified based on their use as agricultural, living, and drinking water and were also classified as pre-monsoon and post-monsoon based on the sampling periods in Table 2. The groundwater is generally colourless, odourless and taste it varies according to the variation of physical factors. pH of water is a very important indicator of its quality, which is controlled by the amount of dissolved Carbon dioxide, carbonates and bicarbonates. An addition of salts to the groundwater may cause rapid rise in pH and the CaCO_3 increases the pH of water making it alkaline (Magdy H.El-sayed, 2012) pH decreases with increasing salinity. In Korea, the pH values of the groundwater samples are within permissible limit such as following ranges; 5.8~8.5 for living water, 6.0~8.5 for agricultural, 5.0~9.0. And in this study, all pH were well suited for the regulation of pH conditions of the groundwater for its usages. The EC of groundwater of the study area ranges from 49 to 1,224 ($\mu\text{S}/\text{cm}$), with the mean value of 294 ($\mu\text{S}/\text{cm}$). The spatial variation of EC in the month of June 2016 and November 2016 is given in the Table 3. The groundwater in all sampling site is not shown the salinity in nature and this is due to the sampling site as isolated patches far from the sea. And, there is not much difference in the EC value between pre-monsoon 2016 and post-monsoon 2016. Especially, EC ranges of living water were narrower than any other water groups so we could guess that in living water less inorganic contents were dissolved in the living water groups. DO is regarded as one of the important factor for defining the groundwater quality but in the law for the preservation of groundwater in Korea the minimum limit for the DO (mg/L) as a agricultural usage is not stipulated as a regulatory article. DO (mg/L) in the usage groups of this study has shown in table 3 the variation patterns of groundwater such as followings; 0.7~8.9 mg/L in agricultural, 0.5~7.5 mg/L in living, 0.6~11.8 mg/L in drinking and seasonal variations from pre-monsoon to post-monsoon were shown 0.5~10.8 mg/L in pre-monsoon, 0.7~11.8 mg/L in post-monsoon. And, reduction potentials also known as redox potentials is measurement tools for the tendency of a chemical species for acquiring electrons and thereby be reduced. In aqueous solutions, reduction potentials is a measurement of property of the solutions to either gain or lose electrons when it is subject to change by introduction of a new species. And also, oxidation/reduction (Redox) reaction potential of groundwater (Eh) plays an important role in the geochemical processes that occur in groundwater. As we know, redox is defined as the transfer of the electrons and redox reactions are enormously important in aqueous environmental geochemistry so the Eh measurements are useful in identifying the redox zones as its value decreases with increases in residence time (D. R. Champ et al 1979). And, it was known that Eh values above 300mV indicate that sulphate would be stable in 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(mV) in groundwater groups have shown the patterns such as followings ; -26.6~697 mV in agricultural, 81.6~513.0 mV in living, -53.0~653.0 mV in drinking and seasonal variations from pre-monsoon to post-monsoon were shown such as following patterns; -9.0~465.0 mV in pre-monsoon, -53.0~697.0 mV in post-monsoon. As shown in the results of ORP in Table 2, it could be inferred that ORP of agricultural area more wider than those of other samples because the inflow of the contaminants source from the agricultural activities and local pollution could affect the groundwater quality in the agricultural area. And also, in this study we tried to compare the distribution of cations and anions. The results showed to be 17.51~68.77 mg/L and 17.63~178.8 mg/L for Na^+ , 2.4~40.99 mg/L and 3.79~124.4 mg/L for K^+ , 8.08~60.34 mg/L and 6.48~62.03 mg/L for Mg^{2+} , and 36.82~229.94 mg/L and 33.65~189.4 mg/L for Ca^{2+} . The distribution characteristics for each type of water usage showed that cation concentration is high in agricultural water while the results were slightly high in October and November when compared to the data for June, July, and September. This data is shown in Table 3. The distribution of five anions, Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , and PO_4^{3-} , was also compared, focusing on the evaluation of groundwater quality. The results showed to be 28.0~512.0 mg/L and 27.00~271.00 mg/L for Cl^- , 19.03~65.0 mg/L and 17.01~98.00 mg/L for SO_4^{2-} , 45.42~431.27 mg/L and 49.27~867.59 mg/L for CO_3^{2-} , and 92.24~875.81 mg/L and 100.06~1761.91mg/L for HCO_3^- , and 0.00~0.00 mg/L and 0.21~0.35 mg/L for PO_4^{2-} . The distribution characteristics showed even distribution for agricultural, residential, drinking, and industrial water, and the data for each sampling period and usage is shown in Table 4.

Table 2. pH, EC, DO, ORP values (Average, Minimum, Maximum) of samples (n=145)

Usage		Items											
		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 (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

Table 3. Na^+ , Ca^{2+} , K^+ , Mg^{2+} values (Average, Minimum, Maximum) of samples (mg/L, n=145)

Usage		Items											
		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

	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
Usage	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
(n=145)	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
Total	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
(145)	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

Table 4. Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , PO_4^{3-} values (Average, Minimum, Maximum) of samples (mg/L, n=145)

		Items														
		Cl ⁻			SO ₄ ²⁻			CO ₃ ²⁻			HCO ₃ ⁻			PO ₄ ³⁻		
Usage		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
Total (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

3.2 Applications of the Graphical Models

3.2.1 Piper Diagram

Being Known, water types from the piper diagram were classified such as followings; 1) water groups that plotted at the top of the diamond is high in both $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{Cl}^- + \text{SO}_4^{2-}$, which results in an area of permanent hardness, 2) the water groups that plotted near left corner is rich in $\text{Ca}^{2+} + \text{Mg}^{2+}$ and HCO_3^- and is the region of water of temporary hardness. 3) water groups that plotted at the lower corner of the diamond is primarily composed of alkali carbonated ($\text{Na}^+ + \text{K}^+$ and $\text{HCO}_3^- + \text{CO}_3^{2-}$). 4) water groups lying near the right-hand side of the diamond may be considered saline ($\text{Na}^+ + \text{K}^+$ and $\text{Cl}^- + \text{SO}_4^{2-}$). Piper diagram are also regarded as a major key factor of for linking the inorganic sources of groundwater and soil textile, so it could be linked to Gibb's diagram and Chadah diagrams. And, the classification types of groundwater are regarded as a major factor for the conjecture of the contamination sources from the upper layers of soils and surface water including stream water, reservoir, lake, sea waters and the classifications of groundwater would be regarded as a important signals for presuming of the main source from chemical fertilizer and manures induced by agricultural activities and by other productive activities on the farm fields. For the classifications of the groundwater by Piper's model, samples were classified for their usages such as drinking, living, industrial shown in Figure 1 and also divided as their sampling periods such as pre-monsoon(June) and post-monsoon(July, September, October)

shown in Figure 2. And the major types of groundwater classifications were divided as Ca^{2+} -(Cl^- - NO_3^-) and Ca^{2+} - HCO_3^- types so it could be known that there might be influenced by some inorganic sources from the upper layers of soils and chemical fertilizers. But, there were no specific differences of water types of the groundwater types between usages groups and sampling period groups.

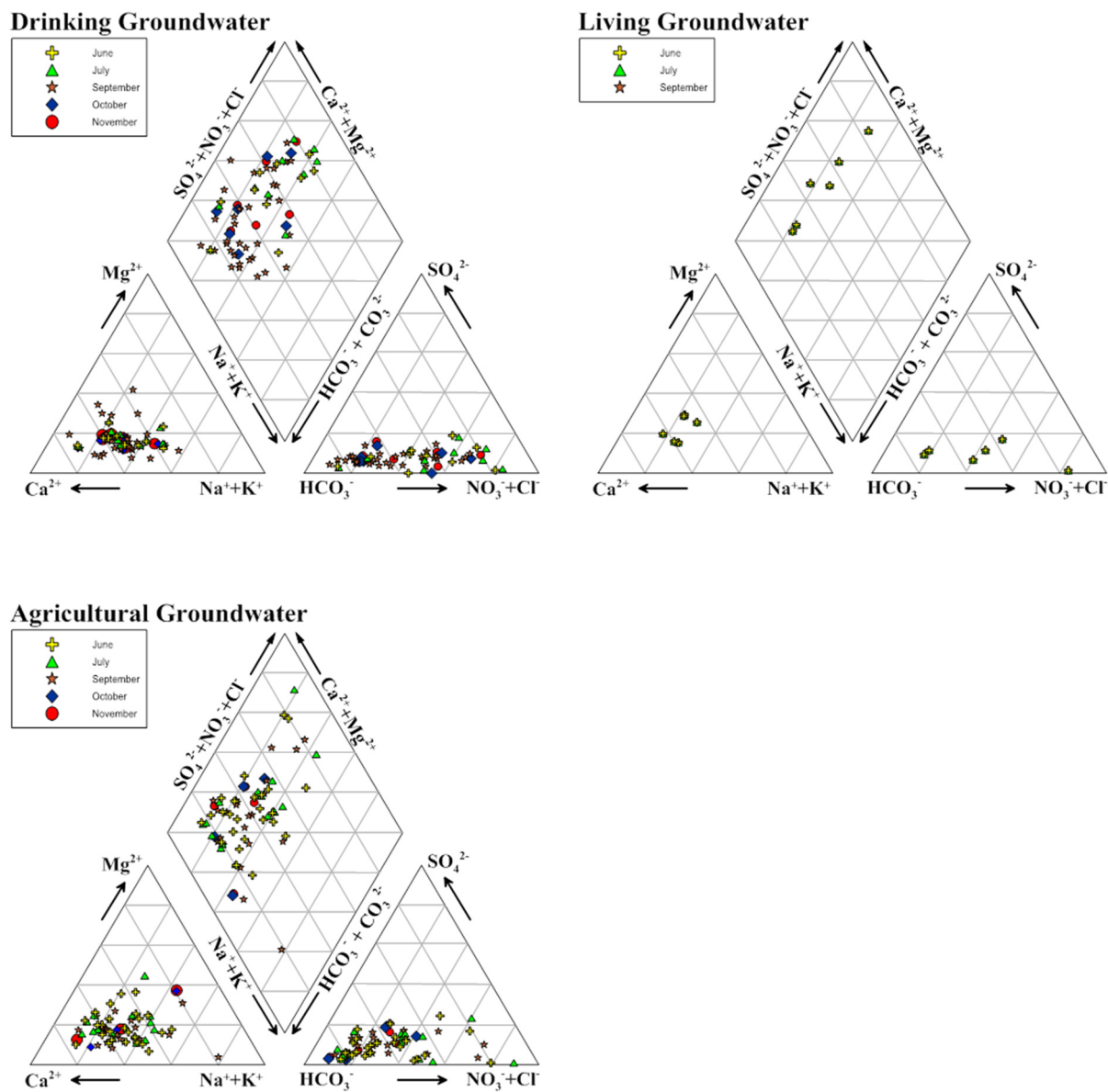


Figure 1. Piper diagram of groundwater grouped by usages

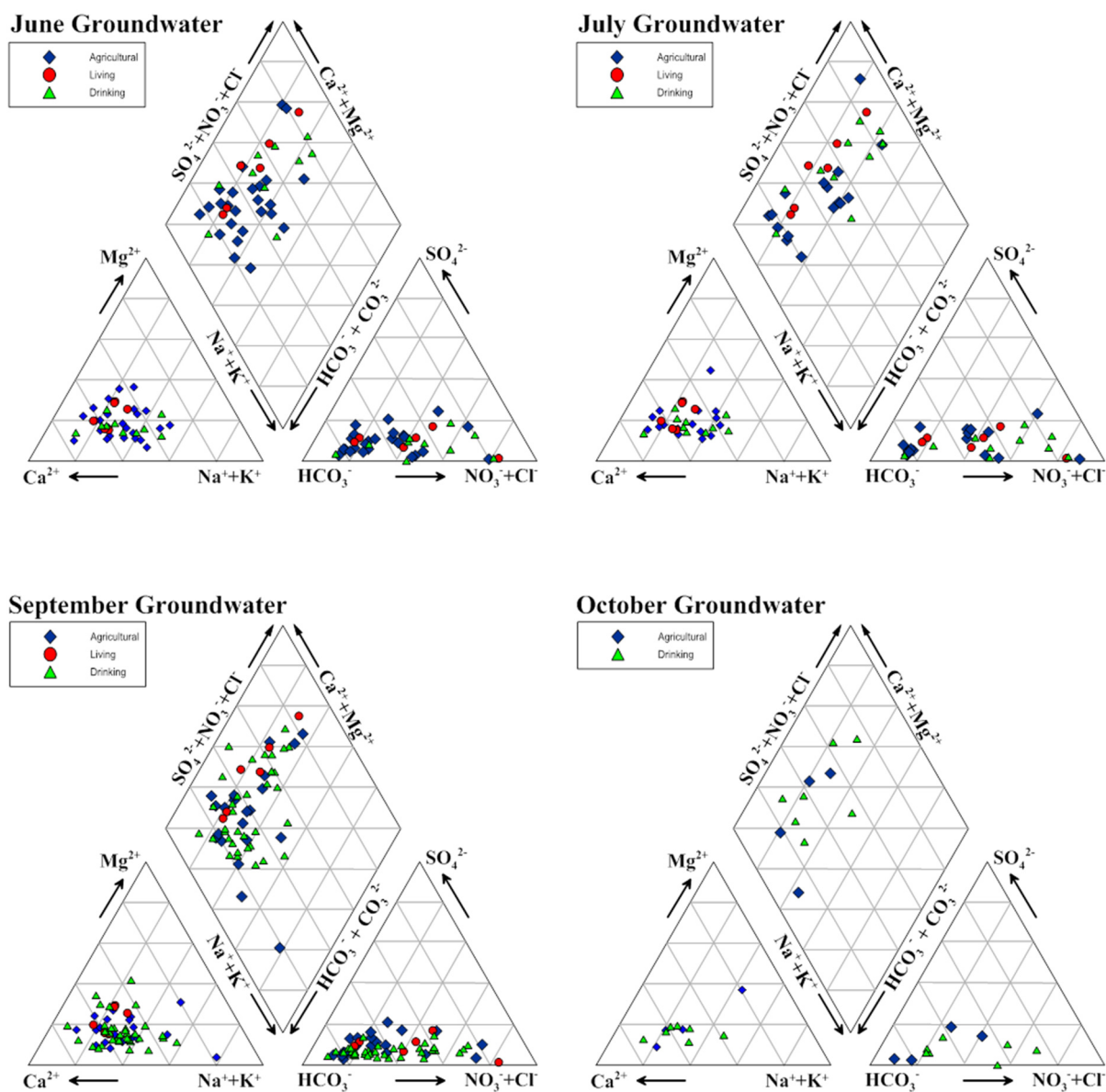


Figure 2. Piper diagram of groundwater for seasonal variation from June to October

3.2.2 Gibbs Diagram

Gibbs proposed a diagram to understand the relationship of the chemical components of waters and classified the groundwater chemistry resulting due to three mechanisms as shown in Figure 3. This plot explains the relationship between water chemistry and aquifer lithology. Such a relationship, help to identify the factors controlling the groundwater chemistry. As most of the points plot in the region of rock water interaction, this is likely to be the dominant process controlling the groundwater chemistry of this area. However, some points also fall in the region near the evaporation, indicating that this process is also responsible for the groundwater chemistry. While the Piper diagram is a method for classifying groundwater based on the distribution of both cations and anions, and the Gibbs diagram is a method for estimating 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 (Total Dissolved Solid). Figure 3 shows the Gibbs diagram based on TDS and the concentration of cations and anions; it shows that most of the cations and anions in groundwater have a rock-dominance origin. This characteristic

indicates the dissolution of ions in groundwater through the interaction between groundwater and rock or soil is more dominant than precipitation or any other sources

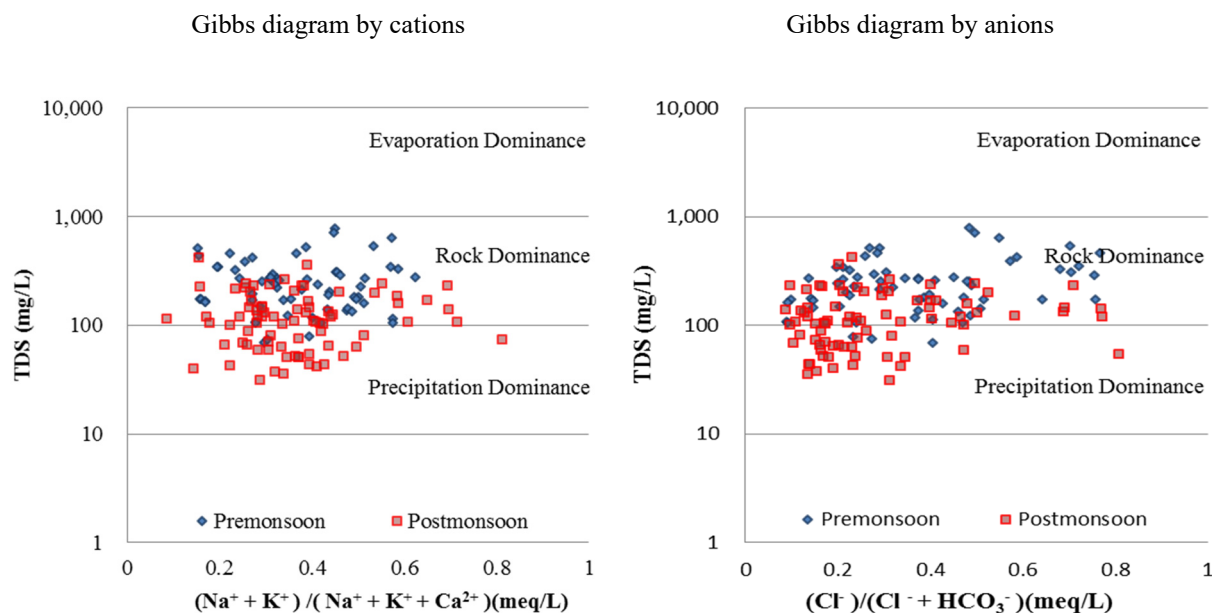


Figure 3. Gibbs diagrams of groundwater by using cations (A) and anions (B)

3.2.3 Chadah Diagram

While the Piper diagram is a method for classifying groundwater based on the distribution of both cations and anions, and the Gibbs diagram is a method for estimating 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 (Total Dissolved Solid). Figure 3 shows the Gibbs diagram based on TDS and the concentration of cations and anions; it shows that most of the cations and anions in groundwater have a rock-dominance origin. This characteristic indicates the dissolution of ions in groundwater through the interaction between groundwater and rock or soil is more dominant than precipitation or any other sources. Unlike Gibbs, Chadha proposed a modified diagram and classified the origin of ions into 8 groups. In Chadha diagram, the square or rectangular field describes the overall ion distribution and character of groundwater for demonstrating geochemical classification and hydrochemical processes of groundwater. In order to define the primary character of groundwater, the rectangular field is divided into eight sub-fields, each of which represents a water types in Table 5. The tracing study of ion based on the Chadha diagram indicated that there is an interaction between the alkaline earths and alkali metals that originate from soil or rock interactions with weak acidic anions and strong acidic anions in groundwater as shown in Figure 4. In Gibbs and Chadha diagram, it was supposed that dominance types of groundwater could be concluded in Gibbs diagram (hydrochemical) and dominance types of component in the specific range would be defined in Chadha diagram (geochemical), so the combination of two diagrams would be regarded as a very convenient tool for illustrating the general types of groundwater in laboratory scales.

Table 5. Geochemical classification and hydrochemical parameters of groundwater (D. K. Chadha, 1999)

Classification groups	Notations	
	Fields	Water types
	1	Alkaline earths exceed alkali metals
	2	Alkali metals exceed alkaline earths
	3	weak acidic anions exceed strong acidic anions
	4	Strong acidic anions exceed weak strong acidic anions
	5	Alkaline earths and weak acidic anions exceed both alkali metals and strong anions, respectively. (Ca-Mg-HCO ₃ type, Ca-Mg-dominant HCO ₃ type, HCO ₃ -dominant Ca-Mg type)
	6	Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions (Ca-Mg-Cl type, Ca-Mg-dominant Cl type, Cl-dominant Ca-Mg type)
	7	Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions (Na-Cl type, Na ₂ SO ₄ -type, Na-dominant Cl type, Cl-dominant Na type)
	8	Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions (Na-HCO ₃ type, Na-dominant HCO ₃ type, HCO ₃ -dominant Na type)

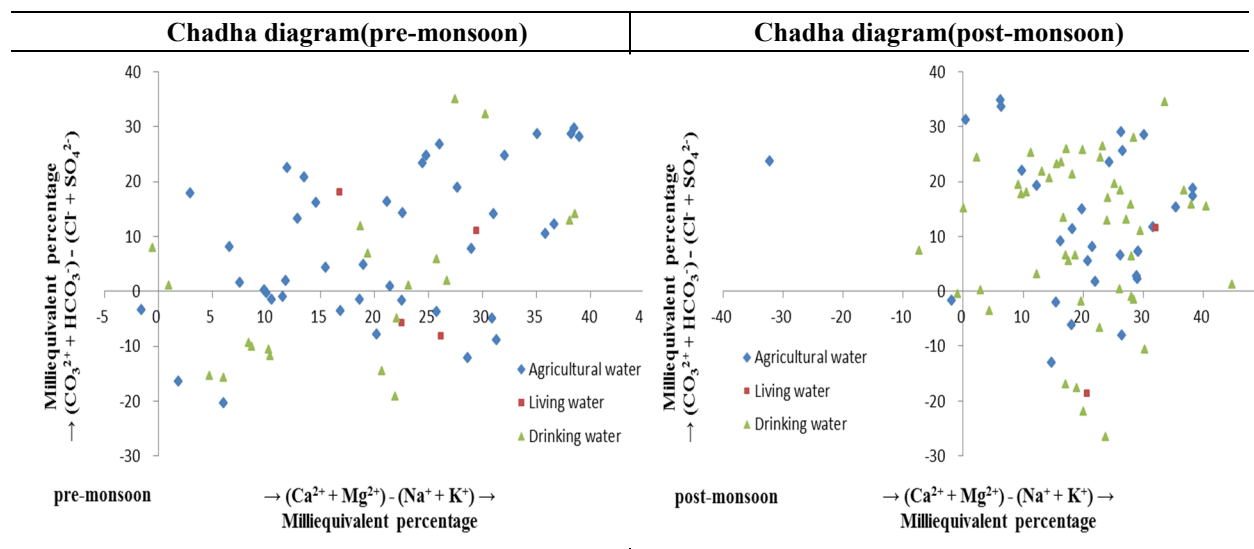


Figure 4. Geochemical classification and hydrochemical parameters of groundwater

3.3 Chloro Alkaline Index

Ion exchange process depends on replacement of adsorbed ions on the exchange complex by ions in solution. Ion exchange is one of the important processes responsible for the concentration of ions in groundwater. Further, to discriminate which ion (Ca^{2+} or Mg^{2+}) controls the hydrochemical reactions, two indices of base exchange (IBE), namely the chloroalkaline indices (CAI1 and CAI2) were estimated and presented below (Ishaku, 2011). The ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the chloro-alkaline indices. To know the direction of exchange during the path of groundwater through the aquifer, Schoeller suggested 2 kinds of chloro-alkaline indices such as CAI 1 and CAI 2 to indicate the exchange of ions between groundwater and its host environment and the ion exchange and reverse ion exchange were known by using chloro-alkaline indices as shown in Figure 5. When there is an ion exchange between Na^+ or K^+ in groundwater with Mg^{2+} or Ca^{2+} in the aquifer material (rock/weathered layer), both of the indices are positive, indicating ion exchange of sodium in groundwater with calcium or magnesium in the weathered

material. While in reverse exchange both indices are negative when there is an exchange of Mg^{2+} or Ca^{2+} in the waters with Na^+ and K^+ in the rocks. So, the ion exchange and reverse ion exchange mechanisms seem to occur in both the directions depending on the groundwater flow path, residence time and chemical processes including carbonates weathering, silicate weathering, evaporation process.

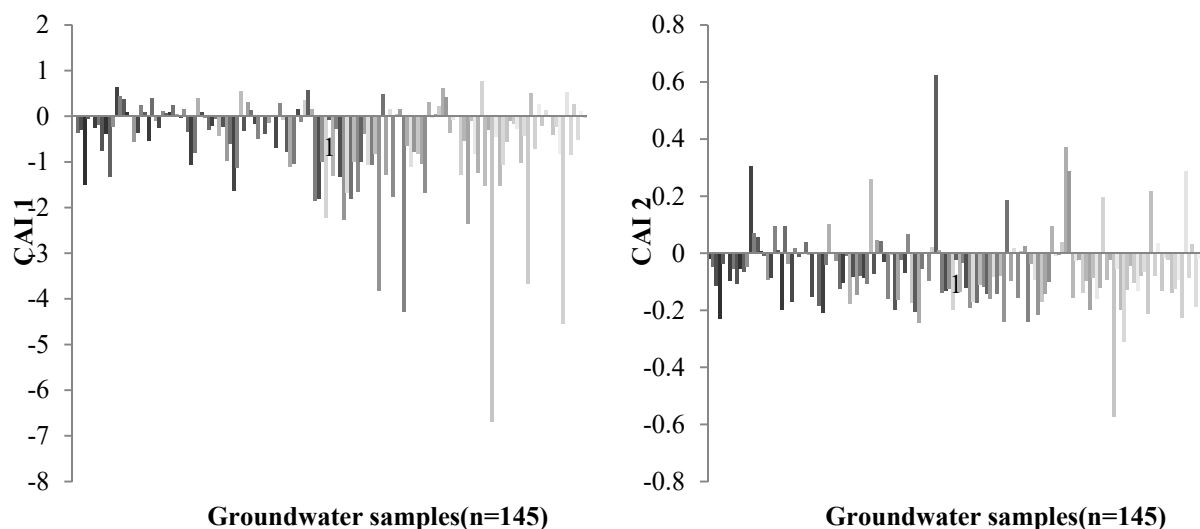


Figure 5. Bar diagram of Chloro Alkaline Indices (CAI 1 and CAI 2) in groundwater samples

3.4 Chemical Evolutions of Groundwater

3.4.1 Carbonate Weathering

Major ions constitute a significant part of the total dissolved solids present in groundwater. The concentrations of these ions in groundwater depend on the hydrogeochemical processes that take place in aquifer system. These processes occur when the groundwater moves toward equilibrium in major ion concentration. Hence, the study of concentration of various major ions present in groundwater is used in the identification of geochemical process. The plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$ will be close to the 1:1 line if the dissolutions of calcite, dolomite and gypsum are the dominant reactions in a system as shown in Figure 6. Ion exchange tends to shift the points to right due to an excess of $\text{SO}_4^{2-} + \text{HCO}_3^-$ (Cerling *et al.*, 1989 and Fisher and Mulican, 1997). If reverse ion exchange is the process, it will shift the points to the left due to a large excess of $\text{Ca}^{2+} + \text{Mg}^{2+}$ over $\text{SO}_4^{2-} + \text{HCO}_3^-$. The plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$ in Figure 7 shows that most of the groundwater samples exceed the 1:1 line, indicating reverse-ion exchange except for few samples distributed on both sides of line that indicate no ion exchange or reverse ion exchange. On the other hand, the points falling along the equi-line ($\text{Ca}^{2+} + \text{Mg}^{2+} = \text{SO}_4^{2-} + \text{HCO}_3^-$) suggest that these ions have been resulted from weathering of silicates of igneous rocks (Datta *et al.*, 1996; Rajmohan and Elango, 2004 and Kumar *et al.*, 2006). Groundwater points, which are placed in the $\text{Ca}^{2+} + \text{Mg}^{2+}$ over $\text{SO}_4^{2-} + \text{HCO}_3^-$ side indicate that carbonate weathering is one of the hydro-geochemical process. And, in Figure 7 both of calcium and magnesium ions increase proportionally with increase of salinity indicating that the carbonate weathering in the aquifer is carried out by chloride sources. The major source of Ca^{2+} are limestone, dolomite, dolomitic limestone, marl and gypsum, whereas the Mg^{2+} sources are dolomitic limestone and dolomite.

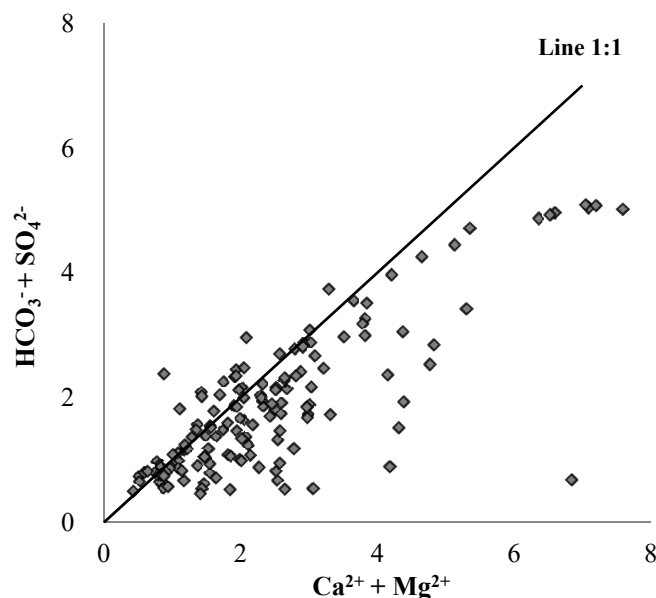


Figure 6. Relation between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{SO}_4^{2-} + \text{HCO}_3^-$ in groundwater samples

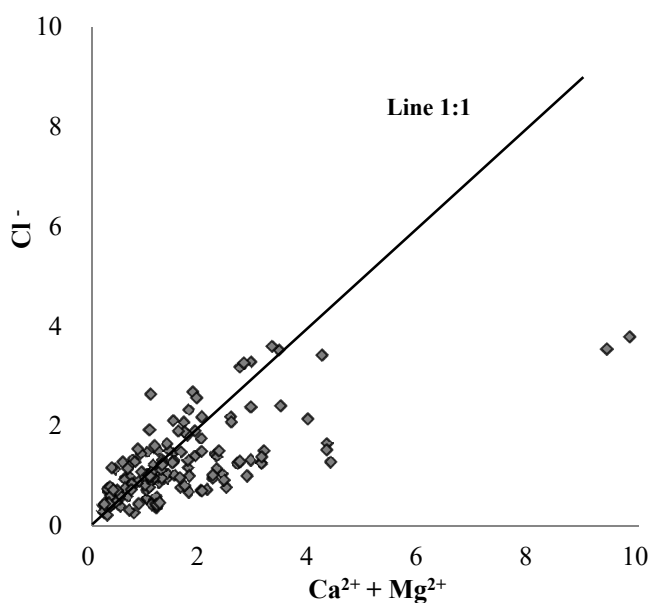


Figure 7. Plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ against (Cl^-) in groundwater samples

3.4.2 Silicate Weathering

Silicate weathering is one of the keys for geochemical processes controlling the major ions chemistry of the groundwater, especially in hard rock aquifers (Kuldip-Singh, 2011). The plot of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio of the groundwater suggests the dominance dissolution of calcite and dolomite that present in the aquifer. That is, if the ratio $\text{Ca}^{2+}/\text{Mg}^{2+} = 1$, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution (Mayo and Loucks, 1995). Higher $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratio >2 indicates the dissolution of silicate from igneous minerals, which contribute calcium and magnesium to groundwater. It can be seen from Figure 8 that the groundwater samples are found near or greater than 2 indicating the effect of silicate minerals (igneous including granite rocks). And, silicate weathering can be understood by estimating the ratio between $(\text{Na}^+ + \text{K}^+)$ and total cations (TZ^+). This indicates that the samples are plotted near the $\text{Na}^+ + \text{K}^+ = 0.5 \text{ TZ}^+$ line shown in Figure 9, reflecting the involvement of silicate weathering in the geochemical processes, which contributes mainly sodium and potassium ions to the groundwater (Stallard and Edmond, 1987). Furthermore, weathering of

soda feldspar (albite) and potash feldspars (orthoclase and microcline) may contribute Na^+ and K^+ ions to groundwater. Feldspars are more susceptible to weathering and alteration than ultrastalte quartz in silicate rocks. The $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ ratio of more than 3 is found in few samples suggesting that silicate weathering occurs in groundwater samples in addition to the carbonate dissolution as shown in Figure 10. Further plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs total cations (TZ^+) groundwater samples, in Figure 11 resulted in a linear spread between $1:2(\text{Ca}^{2+} + \text{Mg}^{2+} = 0.5 \text{ TZ}^+)$ line and $1:1$ equil-line indicating that some of these ions ($\text{Ca}^{2+} + \text{Mg}^{2+}$) are resulted from the weathering of silicate minerals.

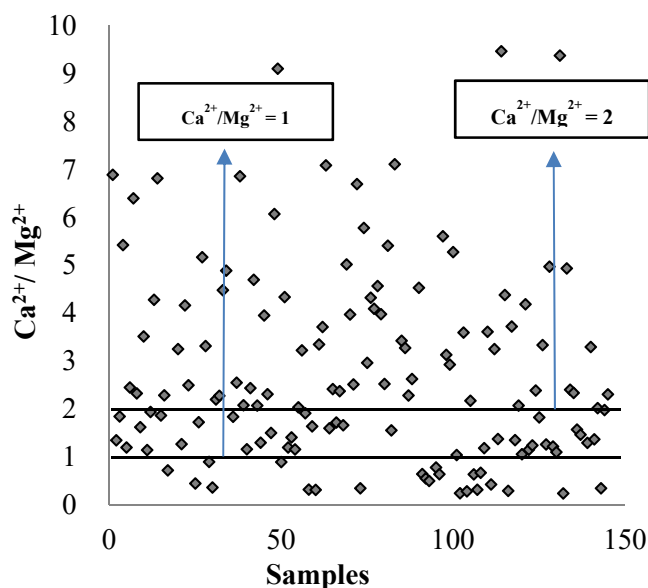


Figure 8. The Scatter diagram of $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratio in groundwater samples

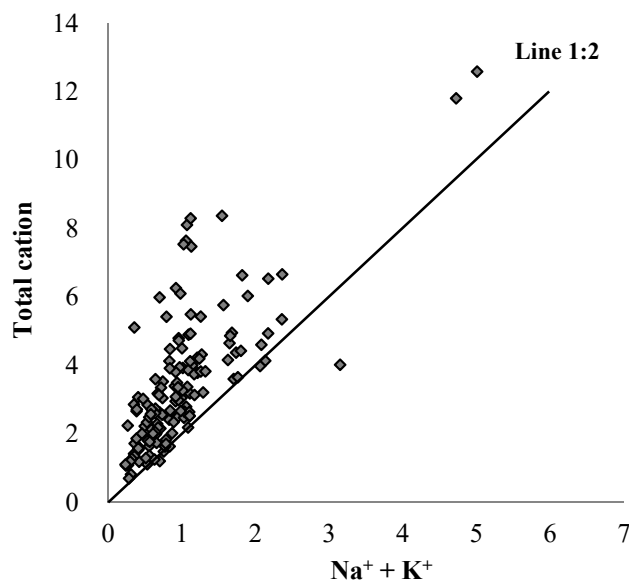


Figure 9. Scatter diagram of $(\text{Na}^+ + \text{K}^+)$ versus total cations (TZ^+)

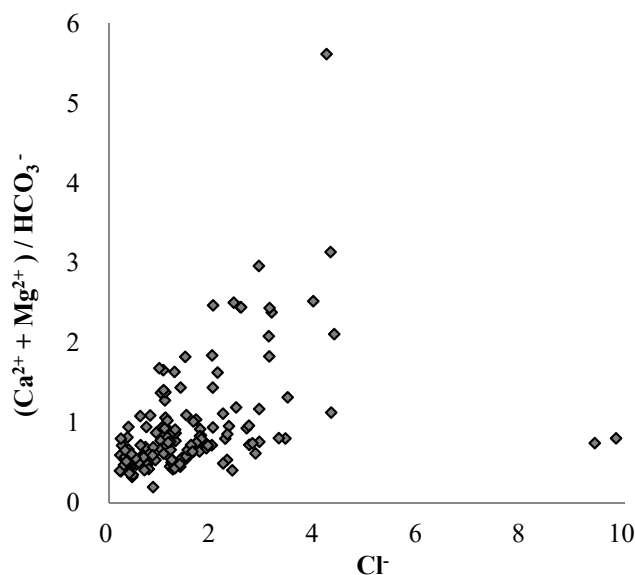


Figure 10. Scatter diagram of $(Ca^{2+} + Mg^{2+})/HCO_3^{-}$ and Cl^{-} (mmol/l).

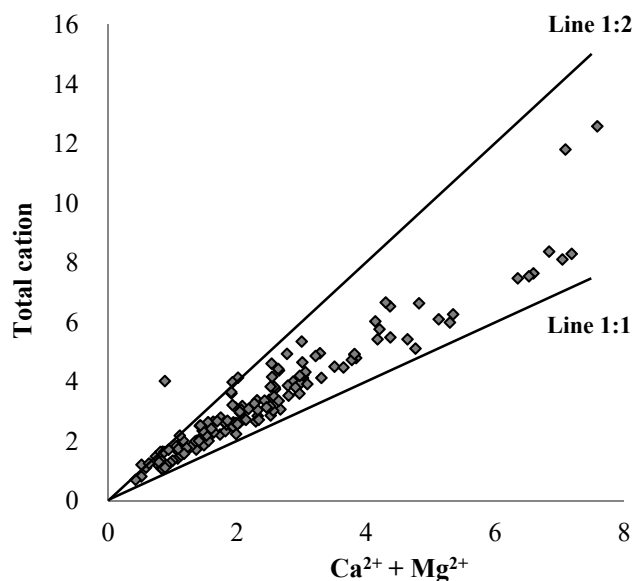


Figure 11. Scatter diagram of $(Ca^{2+} + Mg^{2+})$ versus total cations (TZ^{+})

3.4.3 Evaporation

In general, the evaporation process causes an increase in concentrations of all species in water. If the evaporation process dominates, assuming that no mineral species are precipitated, the Na^{+}/Cl^{-} ratio would be unchanged (Jankowski and Acworth, 1997). If halite dissolution is responsible for sodium, the Na^{+}/Cl^{-} molar ratio should be approximately equal to one, whereas a ratio greater than one is typically interpreted as Na^{+} released from a silicate weathering reaction (Mayback, 1987). The trend of EC versus Na^{+}/Cl^{-} scatter diagram of the groundwater samples shows that the trend line is inclined, which indicates that evaporation may not be the major geochemical process controlling the chemistry of groundwater as shown in Figure 12. To confirm that, the diagrams of Gibbs(1970) were done to show the hydrochemical processes of the chemical components of waters from their respective aquifer lithologies and log (TDS) versus $(Na^{+} + K^{+})/(Na^{+} + K^{+} + Ca^{2+})$ and Log TDS versus $Cl^{-}/(Cl^{-} + HCO_3^{-})$ were plotted for groundwater samples Figure 3 and Gibbs diagram allows the distinction between waters controlled by rock dominance and precipitation. And, a plot of Na^{+} vs Cl^{-} concentration of

groundwater of the study area with 1:1 line is given in Figure 13. The sample points fall above and below the 1:1 line and the sample points plotting below the 1:1 line indicate the depletion of sodium with respect to chloride. Similarly, the sample points plotting above the 1:1 line indicate the increase of sodium with respect to chloride. Both the process shows the evidence of cation exchange process (Jankowski and Acworth 1997; Salama 1993). Excess of Ca^{2+} and Mg^{2+} in groundwater may be due to the exchange of Na^+ in water by Ca^{2+} and Mg^{2+} in clay particle such as equation (5) and (6).

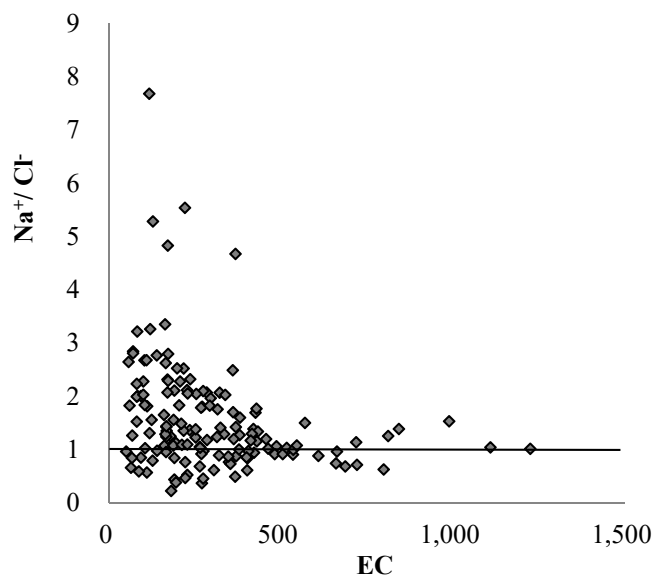
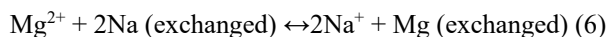
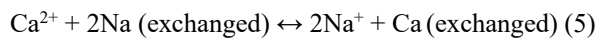


Figure 12. Plot of $\text{Na}^+ / \text{Cl}^-$ ratio versus electrical conductivity (EC) in groundwater samples

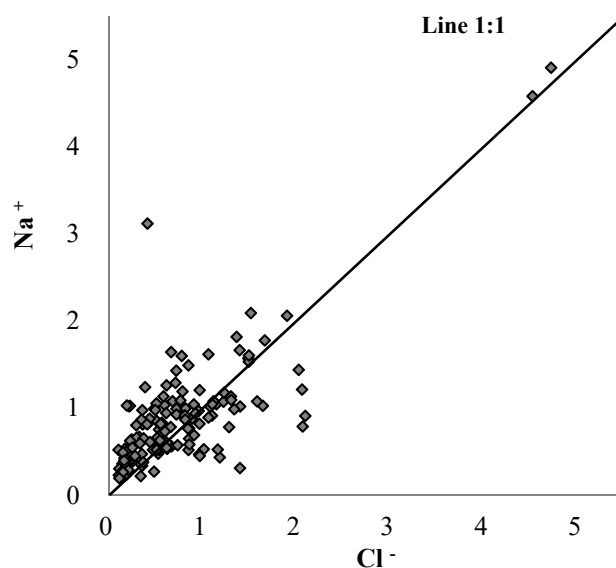


Figure 13. Scatter diagram of Na^+ & Cl^- ratio in groundwater samples

4. Discussion

The objective of this study is concerned with the influences and variations of hydrochemical processes on groundwater through the study of the geochemistry of 145 groundwater samples sampled in pre-monsoon and post monsoon in 2016. So, the major goals of this study were classified as four categories such as followings; on-site monitoring of groundwater qualities by instrumental and laboratory experiment, classifications of groundwater by using of Piper, Gibbs and Chadah diagram methods, tracking of the origins of anions and cations by using of rock-dominance types. The classifications of groundwater based on the Piper diagram showed that the groundwater type is grouped as the Ca^{2+} -(Cl^- - NO_3^-) and Ca^{2+} - HCO_3^- type groups and these types are known as the general features of groundwater in Korea. And, gibbs diagram based on TDS and the concentration of cations and anions has shown that most of the cations and anions in groundwater have a rock-dominance origin. This characteristic indicates the dissolution of ions in groundwater through the interaction between groundwater and rock or soil is more dominant than precipitation or any other sources. The tracing study of ion based on the Chadha diagram indicated that there is an interaction between the alkaline earths and alkali metals that originate from soil or rock interactions with weak acidic anions and strong acidic anions in groundwater. Through Gibbs and Chadah diagram, it was supposed that dominance types of groundwater could be concluded in Gibbs diagram and dominance types of component in the specific range would be defined in Chadah diagram, so the combination of two diagrams would be regarded as a very convenient tool for illustrating the general types of groundwater in laboratory scales. Through the CAI 1 and CA 2, the ion exchange and revers ion exchange mechanisms seem to occur in both the directions depending on the groundwater flow path, residence time and chemical processes including carbonates weathering, silicate weathering, evaporation process. Through the applications of carbonate weathering, silicate weathering, evaporations diagrams further study need to be done to know the exact mechanism between groundwater and rock-soils because groundwater chemistry is guided by lithological influences on water chemistry by complex weathering process, ion exchange along with of other anthropogenic sources.

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