



MASTER'S THESIS OF NATURAL SCIENCE

Characterization of Groundwater Hydro Geochemistry in Granitic Urban Area, Daejeon, Korea

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Graduate School of Seoul National University

College of Natural Science

School of Earth and Environmental Sciences

Hye-Na Ko

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Hye-Na Ko

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Examiner

ABSTRACT

As demand on groundwater increases, it is necessary to manage groundwater quality properly for appropriate use and resource development. Prior to that, figuring out hydro geochemical processes impacting groundwater chemistry has to be done. Especially, hydro geochemical properties of groundwater can be effected by various factors such as mineral reactions and human activities, so systemic study has to be conducted for better understanding of aquifer system. In this study, quantitative like conventional geochemical analysis, and multivariate statistical analysis and qualitative approaches like geochemical modeling were applied to elucidate hydro geochemistry of granitic urban area. Consequently, the conceptual model explicating groundwater system was proposed and results were verified with strontium isotope ratios. Interactions between mineral and groundwater is major contributor of groundwater chemical composition formation, particularly silicate minerals which transform into stable clay minerals that induce ion exchange inside groundwater. Also human activities like agricultural activities and land use patterns threatened groundwater quality. Verified by natural tracer, conceptual model shows that groundwater chemistry evolves from Ca-HCO3 type to Ca(Na)-HCO3 and mixed type (Ca-Cl) with active water-rock interactions and inputs of contaminants from anthropogenic sources. Thus, results of the study will be helpful to fully understand the hydro geochemical system of aquifer in Daejeon city. Additionally, conceptualized aquifer system proposes a way for efficient management of water quality and predicts how the chemical composition changes occur inside the groundwater as well.

Keywords: hydro geochemistry, multivariate statistical analysis, geochemical modeling, conceptual model

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1 INTRODUCTION

1.1 Research Background

Groundwater is one of the most important water resources that human being can use permanently with appropriate managements, and the importance of its increases nowadays due to the climate changes like frequent floods and droughts. The role in sustainable development of groundwater resource requires understanding their origin and renewability (Morán-Ramírez et al., 2016), therefore, assessment of processes affecting groundwater chemical characteristics is crucial for effective water resource management and protection.

Chemical composition of groundwater, or quality of it, is a key factor for determining water purpose like domestic, industrial, and agricultural (Edmunds et al., 2002; Esteller et al., 2012), thus importance of understanding groundwater chemistry increases for sustainable resource management. And groundwater quality is known to be controlled by various factors including precipitation, geological structure, aquifer mineralogy, and anthropogenic activities like leaching of fertilizers. In this case, hydro geochemistry helps in understanding groundwater chemical system providing valuable information related to determine origin of chemical components, transit time, flow patterns (Morán-Ramírez et al., 2016), and hydro-geochemical processes like interaction between aquifer matrix and groundwater. Hence, various studies have been conducting to comprehend and characterize complex hydro geochemical systems of aquifer combining with knowledge of geological and hydrological settings (Hosono et al., 2020; Luo et al., 2018; Martínez & Bocanegra, 2002; Taucare et al., 2020; X. Wu et al., 2020).

For proper understanding aquifer system in view of hydro geochemistry, systemic approaches will be needed to take into account many factors as mentioned earlier affecting chemical compositions of groundwater. Accordingly, to describe hydrogeochemical processes while groundwater flow, quantitative approaches like ionic ratio (Subba Rao et al., 2022; Zaidi et al., 2015; Zakaria et al., 2021), and multivariate statistical analysis (Mohamed et al., 2022; Pathak & Limaye, 2011; Sahu et al., 2018; Sikakwe et al., 2020) were widely used. Also recent studies tried to suggest conceptual model characterizing entire hydro geochemical processes combining quantitative description with conventional approaches (Chen et al., 2021; Marghade, Malpe, & Subba Rao, 2021; Pérez-Ceballos et al., 2021; Roy et al., 2020; Subba Rao et al., 2017), and one of the most well-known techniques is mass transfer simulation that can quantifying mineral reactions using geochemical codes like NETPATH (Plummer et al., 1994) or PHREEQC (Parkhurst & Appelo, 2013). The soundness or validity of simulation results depends on reliability of the basic hydro chemical concepts and principles, accuracy of data that put into model, and degree of grasping hydro geochemical processes in the study area (Güler & Thyne, 2004). So studies attempting to combine simulation results have been conducted to evaluate hydro geochemical processes with qualitative approaches prior to modeling.

Those mass transfer simulation modeling programs only take into consideration water rock interaction, or natural process, so they are useful to depict mineralization processes that cause chemical composition difference between two points along the flow path. However, groundwater quality is affected and will be continuously influenced by anthropogenic factors like population growth, massive agriculture development, industrialization and urbanization in the present era and future as well. Thus, it is more and more crucial to figure out and reflect factors related to human activities when assess the hydro geochemical processes for conceptualize the groundwater system.

Studies trying to conceptualize the groundwater system conducted mineralization quantifying simulation with geochemical modeling program. However, the problem is that they use quantified results for interpreting geochemical data and suggesting conceptualized results without verification, whether results can explain the chemical composition changes properly or not. It means that lots of previous studies didn't take into account anthropogenic causes that can't be reflected on simulations. Also there is little hydro geochemical researches targeted at domestic environment combining different points of view like qualitative and quantitative descriptions.

1.2 Objectives and Scope

The main purpose of this research is to suggest conceptual model of groundwater system in granitic urban area in Korea by combining qualitative and quantitative approaches for characterizing hydro geochemistry. Integration of hydro-geochemical study and characterization of groundwater geochemistry can be used for construction of conceptual model describing aquifer system with evolution processes. Furthermore, additional natural tracer (strontium isotope analysis in regional scale) suited with geological and surrounding conditions will be applied for validating modeling results and evaluating whether the quantified results can actually explain aquifer system properly in respect to both natural and anthropogenic factors or not. Attempting to characterize hydrogeochemical characteristics with systemic approaches in diverse perspectives and validating analysis, this study aims to propose a more sophisticated conceptual model explaining groundwater chemistry for sustainable resource management.

2 STUDY AREA

The study area is located in Daejeon city, South Korea (Fig. 2-1). The geological condition of Daejeon area was surveyed by several researches, and according to those studies, study area is composed of Jurassic plutonic rocks like two-mica granite, biotite granite, and schistose granite (Park et al., 1977; Lee et al., 1980) (Fig. 2-1a). And plutonic rocks intruded into Pre-Cambrian or Paleozoic metamorphic rocks of the Ogcheon belt, including partial metamorphosed sedimentary deposits (Jeong, 2002; Hwang, 2013). Quartz porphyry and aplite dykes intrude the Jurassic granite throughout southern part of the study area as well. Weathered zones of granite are developed widely and deeply and the thickness of weathered zone ranges from 20 m to 50 m (Lim et al., 1982). The mean annual temperature of study site for 10 years is about 13.2 °C and precipitation is about 1300 mm (Korea Meteorological Administration, <u>www.kma.go.kr</u>). Both temperature and precipitation rapidly increase in August, Korean monsoon season. High lands are formed in north-western and south-eastern part, where the topographical elevation varies 300 m to 573 m above the sea level (Fig. 2-1b). Three major urban rivers (Yudeung, Daejeon, and Gap stream) are developed on the central part of the city, so the groundwater flows from higher elevation area to the streams developed on alluvium deposits. Furthermore, land uses of the study area are classified into 58 % of forest, 22 % of agriculture land, and 20 % of urban (industrial, residential area).



Figure 2-1 Description of the study area, Daejeon city, South Korea; (a) shows the geological condition and (b) shows the elevation (m, a.s.l) and flow direction of groundwater in the Daejeon city.

3 METHODOLGY

3.1 Water Sampling

Groundwater samples were collected 131 wells in the study area, and those were located at various sites like schools, parks, apartment complexes, and industrial complexes for various purposes. Additional samples for updating data were also collected from newly installed 8 wells used as emergency water supply facilities throughout Yuseong area for 3 times during 2021. Figure 3-1 shows the location of wells, and additional 8 wells are depicted as red color. Surface water sample was also collected at Gap stream for the comparison. All samples were collected in 2-L polyethylene bottles after stagnant water was removed by pumping for at least 15 minutes and parameters were stabilized. Temperature, electric conductivity (EC), total dissolved solids (TDS), and pH were measured directly using YSI ProDSS digital sampling system (Xylem, USA). Collected samples were filtered through 0.45-µm membrance and stored in refrigerator until the measurement. Major cations and anions were measured using ion chromatography (ICS-5000; Thermo Scientific Dionex, USA) and all measurements were carried out at the Korea Basic Science Institute (KBSI). Charge balance error (CBE) were calculated for all samples and retained samples with CBE less than $\pm 10\%$. Generally, common practice is to exclude samples with CBE's of $\pm 5\%$ (e.g. Freeze and Cherry, 1979), but we followed the cases with CBE's of $\pm 10\%$, taking into consideration a systemic error that can be induced by the analytical techniques (Güler et al., 2002; Pacheco Castro et al., 2018). For the strontium isotope ratio (87Sr/86Sr), Neptune MC-ICP-MS instrument (Thermo Finnigan, Bremen, Germany) at KBSI was used, and less than 1ng of negligible Sr^{2+} in all procedural blanks contained. The $^{87}Sr/^{86}Sr$ ratios were normalized to 0.1194 of $^{86}Sr/^{88}Sr$ (Faure, 1977), and the mean isotopic ratio of NBS987 (U.S. National Bureau of Standards) was 0.710247 \pm 0.00017 (2 σ , n=18).



Figure 3-1 Sampling points: location of wells and surface water sampling point

3.2 Principal Component Analysis (PCA)

Multivariate statistical analysis was performed to back evolution of groundwater quality identified from conventional hydro geochemical analysis up, Principal Component Analysis (PCA), or linear display method, was applied, and this allows to figure out associations between variables by reducing the dimensionality of large data set. In this study, major ions (Ca²⁺, K⁺, Mg²⁺, Na⁺, HCO₃⁻, Cl⁻, NO₃⁻ and SO₄²⁻) were used in analysis. Parameters like temperature and DO were excluded due to the absence of meaningful change during research periods and pH also were excluded. Because they are redundant with other factors (e.g. pH strongly correlates with bicarbonate). Then Shapiro-Wilks test was performed to check whether the selected data follows Gaussian distribution or not. After that, data were normalized to zero mean and unit variance for avoiding misclassifications caused by difference of unit or order of magnitude of each parameter. This normalized process also known as standardization (z-scale). For reducing the dimension of treated data set, correlation matrix of the original data set is diagonalized, transforming variables into uncorrelated (orthogonal) ones called principal components (PCs). The eigenvalues of the PCs are indicators of their associated variance. And the participation of original parameters in the PCs is provide as "loading" and the individual transformed observations are "scores" (Helena et al., 2000). After that, varimax rotation, which can extract PCs with eigenvalue>1 by Kaiser criterion for interpretation (Kaiser, 1958), was applied. All statistical processes were performed by using R (R Studio version 1.4.1717).

3.3 Geochemical Modeling

PHREEQC is written in C++ and developed by the United State Geological Survey (USGS). This program is designed to perform various kinds of reaction related to geochemical calculations. This can handle various types of aqueous models and can calculate (1) speciation and saturation index, (2) one dimensional transport calculation with reversible and irreversible reactions, and (3) mass transfer calculation (Parkhurst & Appelo, 2013). In this study, PHREEQC was used to calculate activity ratio of dissolved components, saturation index (SI) of mineral, and mass transfer simulation along the groundwater flow path.

3.3.1 Thermodynamic Calculation

Groundwater chemistry was governed by various processes, such as flow, recharge and discharge processes and fluid-rock interactions. In long residence time, groundwater flows along the flow path, the chemical composition of groundwater is generally effected by weathering processes of minerals. Saturation index (SI) is useful indicator predicting the reactive mineralogy of subsurface from groundwater data without collecting samples of the solids or analyzing the mineralogy. Also SI can indicate the state of mineral inside the groundwater by its sign. Saturation index can be written by Equation 3-1.

$$SI=Log(IAP/K_{sp})$$
 (Eq. 3-1)

where IAP is derived by multiplying the ionic activity values of dissolved ion species, and K_{sp} is equilibrium constant of the minerals.

If SI values equals to 0, it means water is equilibrium with respect to mineral. When SI is greater than 0, water is saturated and mineral can be precipitated into the water. When SI is lower than 0, water is unsaturated and mineral can be dissolved into the water.

3.3.2 Inverse Modeling

Inverse modeling is one of the most well-known simulation methods. This simulation has been widely applied to hydrology researches to evaluate the hydro geochemical evolution related to chemical reactions determining chemical compositions of groundwater. Lastly, this can quantitatively calculate mass transfer of minerals from recharge point to discharge point on the same flow path. the mass balance of conceptual models is expressed as Equation 3-2.

$$\sum_{j=i}^{n} a_{ij} x_j = b_i \quad (\text{Eq. 3-2})$$

where a_{ij} is the stoichiometric number of element *i* in mineral *j*, x_j is the molar number of specific minerals of gases that dissolved or precipitated, and b_i is increment of element *i* in the final solution compared with the initial solution (Li et al., 2010).

Positive values represent dissolution of mineral or gas phases, and negative values indicate precipitation of mineral or gas phases. According to the simulation results, we can quantify key geochemical processes which can account for the observed changes in chemical composition between two points along the groundwater flow (L. Niel Plummer et al., 1990; L N Plummer et al., 1994).

4 RESULTS AND DISCUSSION

4.1 General hydro geochemical characteristics

The statistical information of physicochemical variables of collected groundwater samples are summarized in Table 4-1. The pH conditions in this study area ranged from 5.9 to 8.6 with small standard deviation, indicating weak acidic and weak alkaline conditions, and those are general ranges appeared in granitic basement rock (B. D. Lee et al., 2019). The EC values varied from 77.6 to 883 µS/cm (mean: 323.8 µS/cm), representing fresh quality of groundwater. TDS values ranged from 73.4 to 569.6 mg/L with average of 106.3 mg/L, and the range showed generally low to moderate values. Among the dissolved ions in groundwater, Ca^{2+} and HCO_3^{-} were most abundant species, and major ions were in the follow order; Ca²⁺>Na⁺>Mg²⁺>K⁺ for cation, and HCO₃⁻>Cl⁻ >SO₄²->Cl⁻ for anion. So, the characteristics of Ca-HCO₃ type can represent hydrogeochemical features of groundwater in this study area, but there were transitions within it (Fig. 4-1). Water type varied from Ca-Na-HCO₃ to Ca-Cl type. Those types of groundwater are generally found in bedrock aquifer in Korea, and indicate interactions or mixing processes between hydro geochemically different compositions (K. H. Kim et al., 2014). Commonly, Ca-Na-HCO₃ type indicates natural water quality in aquifer system formed by enrichment of sodium by water-rock interactions like silicate mineral weathering or ion exchange processes (Chae et al., 2006, 2007). Groundwater with Ca-Cl type represents existence of contaminations from anthropogenic sources like application of chemical fertilizers and sewage leading to increased Cl⁻, SO_4^{2-} , and NO_3^{-1} in groundwater (J. Y. Hwang et al., 2017; P. J. S. Kumar, 2014; Prasanna et al., 2010).

Variables	Max.	Min.	Mean	SD
(n=131)				
T(°C)	22.9	13.6	16.8	1.5
pН	8.6	5.9	6.7	0.5
EC (µs/cm)	883.0	77.6	323.8	173.0
TDS (mg/L)	30.3	0.0	6.6	6.1
Ca^{2+} (mg/L)	115.0	6.6	39.9	22.3
Mg^{2+} (mg/L)	28.8	0.5	6.3	4.3
Na ⁺ (mg/L)	71.2	3.5	19.2	11.0
K ⁺ (mg/L)	11.2	0.4	2.0	1.7
HCO_3^- (mg/L)	326.5	12.2	90.0	52.4
Cl ⁻ (mg/L)	104.0	1.1	31.5	24.9
SO_4^{2-} (mg/L)	186.9	0.1	30.1	27.3
NO_3^- (mg/L)	134.0	0.0	29.0	26.8
SiO ₂ (mg/L)	25.5	2.4	14.7	5.0

 Table 4-1 Statistical summary of hydro geochemical data of sampled groundwater in study area



Figure 4-1 Piper plot that depicts Geochemical face (water type) of the groundwater in the study area

Figure 4-2 shows mechanism controlling the chemistry of groundwater in the study area as Gibbs plot (Gibbs, 1970) by plotting TDS versus $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$. Plot is divided into 3 mechanisms; evaporation, precipitation, and water-rock interaction domains. All samples are plotted on the water-rock interaction domain, which means that interaction between groundwater and aquifer matrix is the major hydro geochemical process governing and determining chemical properties of groundwater in this study area.



Figure 4-2 Mechanism of controlling groundwater chemistry in the study area

4.2 Evaluation of multiple factors governing water quality

4.2.1 Hydro geochemical process

According to the section 4.1, major process that control groundwater quality is interaction between groundwater and aquifer matrix, which plays crucial roles and is useful tool for understanding genesis of groundwater quality. Ca²⁺ and Na⁺ for cation, and HCO₃⁻ and Cl⁻ for anion are both important components that determine water type in this study area. Concentration ratios of dissolved ions were depicted on bivariate plots for distinguishing sort of weathered rocks with taking into account geological condition of the study area.

The (Ca²⁺+Mg²⁺) versus total cations (TZ⁺= Ca²⁺+Mg²⁺ + Na⁺+K⁺ in meq/L) plot (Fig.4-3a) lie below the equivalent line indicating that there is large contribution of alkali metal ions to forming total cations concentration (TZ⁺). Also two reference lines indicate 1:1 and 2:1 of alkaline earth metal ions and TZ⁺, most of the samples are plotted between those lines explain that reactions with silicate minerals may be responsible for supplying Ca²⁺ and Mg²⁺ in groundwater (M. Kumar et al., 2009). The depleted rest should be balanced by other cations, or alkali metal ions. The equivalent ratio between Ca²⁺ and HCO₃⁻ is 1:2 and 1:4, if in silicate terrain, Ca²⁺ and HCO₃⁻ are solely derived from dissolution of calcite and dolomite respectively (Veizer & Mackenzie, 2003; Holland, 1978). Majority of samples are plotted on silicate weathering domain, and some samples are in calcite dissolution zone. According to the geological map (Fig 2-1), there is little carbonate mineral in granitic bedrock area, and if exists, calcite as fracture filling mineral is common (Kim et al., 2007). However, weathering rate of calcite is 120 times faster than silicate minerals, so it is possible to supply Ca²⁺ and HCO₃⁻ ions into groundwater. In other words, even relatively small portion of calcite in aquifer matrix can significantly influence the water chemistry (Meybeck, 1987).



Figure 4-3 Relation between Ca^{2+} , Mg^{2+} , HCO_3^- , and total cations concentration (TZ^+)

According to the relation between TZ^+ and concentration of alkali metal ions, most of the samples are plotted below the $Na^++K^+= 0.5TZ^+$ line (Fig.4-4a). This observation indicates involvement of silicate mineral weathering and/or soil salts is significant for suppling alkali metal ions into groundwater in this study area (ref). Figure 4-4(b) shows Na^+ versus Cl⁻ in water samples, some of samples are plotted below the equivalent line. This indicates the situation of excessive Na^+ comparing to Cl⁻, which infers that weathering of Na-bearing silicates like albite is main source for Na^+ . Whereas some of the samples that are plotted over the equivalent line indicate excessive Cl⁻. However, there is no known geological information for existence of halite in this study area, so Cl⁻ in groundwater is hard to derived from geological source. Representative sources for anthropogenic Cl⁻ in groundwater include animal waste, chemical fertilizers, domestic sewage, and leachate from landfill (Nagarajan et al., 2010; Tay, 2021).



Figure 4-4 Relation between Na⁺, K⁺, Cl⁻, and total cations concentration (TZ⁺)

Figure 4-5(a) shows bivariate plot of sum of alkaline earth metal ions concentration versus HCO₃ and SO₄²⁻. According to the plot, most of the samples are plotted above the equivalent line, meaning that large amount of Ca²⁺ or Mg²⁺ can be derived from non-carbonate sources and over plus charge by those ions might be balanced by other anions like Cl⁻ from anthropogenic inputs (Srinivasamoorthy et al., 2008; Varol & Davraz, 2014). Moreover, dominance of Ca²⁺ and Mg²⁺ over HCO₃⁻ and SO₄²⁻ can be result of ion exchange, which is defined by the process that alkali metal ions like Na⁺ and K⁺ in groundwater might be exchanged with Ca²⁺ or Mg²⁺ from aquifer matrix such as clay minerals (J. Y. Hwang et al., 2017; Rajmohan & Elango, 2004; Srinivasamoorthy et al., 2014; Zaidi et al., 2015). The relation between (Ca²⁺⁺Mg²⁺-HCO₃-SO_{4²⁻}) versus (Na⁺-Cl⁻) also support the ion exchange process inside the aquifer. If ion exchange process is the dominant process in the system, then the sample should form a linear relation between (Ca²⁺⁺Hg²⁺-HCO₃-SO_{4²⁻}) and (Na⁺-Cl⁻) with a slope of -1 (Rajmohan & Elango, 2004). Linear relation between two variables from figure 4-5(b) is -1.02, which also verified with the hypothesis that ion exchange actually affects quality of groundwater in the study area.

Figure 4-5 Bivariate plots show the interrelation between dissolved components: (a) alkaline earth metal ions versus ($HCO_3^{-}+SO_4^{2-}$), and (b) ($Ca^{2+}+Mg^{2+}-HCO_3-SO_4^{2-}$) versus (Na^+-Cl^-)

Lastly, thermodynamic calculation using geochemical modeling codes, PHREEQC, was conducted. Firstly, mineral stability diagrams delimitating the most stable silicate phases in the fluid are used to study weathering process of silicate minerals (Garrels, 1965). Especially in case of silicate minerals that consist most of the bedrock in this study area, favor incongruent dissolution retaining part of the silica released thorough formation of authigenic minerals, whereas other minerals like carbonates undergo congruent dissolution (Appelo & Postma, 1993; Walraevens et al., 2018). The activity ratios for Na⁺, K⁺, Ca²⁺, and H₄SiO₄ were calculated using the geochemical modeling software PHREEQC (Parkhurst & Appelo, 2013).

Figure 4-6 shows the stability diagram for Na-, K-, and Ca-system. According to that, most of the samples are plotted on the kaolinite and montmorillonite field, and a few lie along the boundary of K-feldspar, muscovite, and microcline field. The fact that most of the water samples in study area are in equilibrium with kaolinite is in agreement with the observation by Freeze and Cherry (1979), concluding that weathering of feldspar or biotite to kaolinite is general process into the granitic bedrock aquifer (Walraevens et al., 2018). Also none of the samples lies on the field of albite and anorthite, which indicates that those are not equilibrium with groundwater, so silicate mineral like anorthite and albite will be decomposed in groundwater. So it is clear that silicates like anorthite and albite undergo chemical weathering when interact with groundwater, with releasing cations and transforming into stable clay mineral forms like kaolinite in groundwater. And weathering of those feldspars must be an important natural factor that controls the hydro chemical evolution of the groundwater in study area.

Figure 4-6 Stability diagram of silicate minerals: (a) Na-system, (b) K-system, and (c) Ca-system

And saturation indices (SIs) of other minerals were calculated using PHREEQC as well. In case of carbonate and sulfate minerals undergo congruent dissolution releasing major ions like Ca^{2+} , HCO_3^- , and SO_4^{2-} . According to the precious studies, SI of specific mineral positively related with the related components (e.g. dissolution of calcite increases concentration of Ca^{2+} and HCO_3^-), dissolution of those minerals is responsible for the increase in dissolved ions (C. Wu et al., 2021). In this study, SIs for calcite, dolomite, gypsum and chalcedony were calculated, and relation between related ions and SI was depicted as bivariate plot, and red colored section in each graph indicates the situation that mineral is under equilibrium state (Fig. 4-7).

Figure 4-7(a) shows relation between Ca^{2+} concentration and SIs of calcite and dolomite. Majority of samples show negative SI value, representing dissolution of calcite and dolomite is responsible for increasing Ca^{2+} in groundwater. However, in case of dolomite, there is little geological source for dolomite, so calcite that exists as form of fracture filling mineral and as main content of sedimentary deposits can be major source for Ca^{2+} and HCO_3^{-} in this study area. In addition, continuous supply of Ca^{2+} into groundwater from Ca-bearing silicate minerals might trigger calcite precipitation and increase SI of calcite, due to the fact that some of the SIs of calcite are near equilibrium state.

Figure 4-7(b) describes relation for SI of gypsum and SO_4^{2-} . Similar to those of carbonates, most of the SIs are indicating unsaturated condition meaning that gypsum dissolution is reliable for supplying Ca^{2+} and SO_4^{2-} in groundwater. Also, other source of SO_4^{2-} might be reaction like oxidation process of fracture filling minerals like pyrite (Cloutier et al., 2008; Glynn & Brown, 2011; H. R. Kim et al., 2019), and human activities like application of chemical fertilizers in agricultural practices (K. Kim et al., 2005; Liu et al., 2020; Roy et al., 2020).

Chalcedony and its SI are known to be used as a measurement of degree of groundwater and silicate mineral reactions (J. M. Lee et al., 2021). SIs of groundwater samples, except for a few, was greater than zero, and those were increased with increasing sum of cations concentration (TZ^+), ensuring that silicate hydrolysis is crucial reaction for formation of cation concentration in groundwater.

Figure 4-7 Saturation indices (SI) of selected minerals: (a) carbonate, (b) gypsum, and (c) chalcedony

4.2.2 Anthropogenic factor in respect to land use

To figure out water controlling factor in the study area, one of the multivariate statistical analysis, principal component analysis (PCA) was conducted on treated raw data. Major ions, physicochemical characteristics (pH, TDS, EC, and total hardness) were included. Table 4-2 shows component weighting, eigenvalue of matrix, and variance of principal components. 3 components explaining 76 % of total dataset were extracted by Kaiser criterion (Kaiser, 1958). To investigate the PC score in respect to the land use and take into account site specificity, or coexistence of urban and forest area, all wells for sampling were classified into 3 categories; residential/industrial, agricultural, and forest area.

The first component, PC 1, representing half of the data is characterized by EC, TDS, and dissolved ions (i.e. Ca^{2+} , K^+ , Mg^{2+} , Na^+ , HCO_3^- , Cl^- , NO_3^- and SO_4^{2-}). EC and TDS both have high loading values meaning that this factor contribute to overall mineralization (Nair et al., 2020). Furthermore, indicator of groundwater contaminations, or Cl⁻ and SO_4^{2-} , also highly load to first components meaning that influence of anthropogenic factors from human activities. According to the spatial distribution for PC 1 (Fig. 4-7a), score of this component is especially higher in residential/industrial area at lower elevation than forest area at higher elevation. indicating that active water-rock interaction exists while groundwater flows from recharge to discharge area. Therefore, the first component reflects multiple sources like anthropogenic, natural and mixed source contributions (Belkhiri & Narany, 2015; Chai et al., 2020; K. H. Kim et al., 2014; Nair et al., 2020; Nakagawa et al., 2021).

The second component, PC 2 explaining 15 % of data set is positively characterized by nitrate. Also score of PC 2 is relatively high at the points of farmland and residential area (Fig. 4-7b), indicating that second factor is defined by anthropogenic factors related to nitrate from contaminations due to absence for geological source for nitrate in study area. Jeong (2003) used δ^{15} N for elucidating source of nitrate in groundwater in Daejeon city, and concluded that contaminant sources of nitrate in study area were leakage from municipal sewage pipe line and septic tanks. So it is reliable that PC 2 is highly related to human activities and contaminants and is correlated with land use.

The last component, PC 3, which explains 11 % of data set, is characterized by negative relation between potassium and silica ion indicating that those species from different sources. General source of SiO₂ in groundwater is from dissolution of silicate minerals which means ion from water-rock interaction (Dobrzyński, 2005; Njitchoua et al., 1997). If potassium is derived from dissolution of silicate minerals like biotite that bear potassium, relation between concentration of potassium and silica ions is proportional. However, in this study, two species are negatively correlated and PC 3 score is much higher in the area classified as residential/industrial area. So PC 3 also indicates contaminants that is different with PC 2, and possible sources for anthropogenic potassium can be road salts, domestic waste, agricultural activities and sewer infiltration (M. Kumar et al., 2009; Raju et al., 2015; Singh et al., 2017). However, according to figure 2-1, the points with high PC 3 score show different geological compositions comparing to other points represented as granitic bedrock. So it is necessary to be clarified the source of potassium, except for anthropogenic sources mentioned above, more in detail with additional sampling.

	PC 1	PC 2	PC 3
pH	0.04	-0.78	0.05
EC	0.97	0.01	0.03
TDS	0.98	0.15	-0.06
Ca2+	0.94	-0.15	-0.04
Mg2+	0.8	0.01	0.18
Na+	0.7	0.19	-0.1
K+	0.31	0.22	0.76
НСО3-	0.68	-0.59	-0.04
Cl-	0.8	0.33	-0.03
SO42-	0.8	0.06	0.13
NO3-	0.37	0.72	0.03
SiO2	0.24	0.23	-0.83
Eigenvalue	5.95	1.78	1.33
Explained %	50	15	11

 Table 4-2 PCA results for selected groundwater quality variables

Figure 4-8 Spatial distribution of each principal component (PC) classified by land use: (a) PC1, (b) PC 2, and (c) PC 3

4.3 Conceptualize the aquifer system

4.3.1 Mass transfer simulation

The hydro geochemical characteristics, ionic ratio plots, and thermodynamic stability diagrams show that the chemical composition and evolution of the groundwater are controlled by interaction between groundwater and aquifer matrix (mineral and rock) with anthropogenic factors like nitrate, and chloride. Quantitative descriptions by simulating inverse modeling in respect to related minerals can be used to back up the findings of this research and also validate the geochemical differences between water types characterized in this study area along the flow path. mass transfer simulation, so called inverse modeling, was conducted with PHREEQC (Parkhurst & Appelo, 2013). On basis of geochemical findings, and geological conditions of the study site, the possible mineral phases were selected for the simulation: calcite, gypsum, albite, anorthite, plagioclase, feldspar, kaolinite, Ca-montmorillonite, illite, and Ion exchange as well. Carbon dioxide gas was assumed to be available along the groundwater flow. Nitrate was excluded in calculation to eliminate influence of anthropogenic factors, and this was reflected when selecting flow path. Flow path according to elevation of the study area was selected from Ca-HCO₃ type as initial water to mixed type as final water, and both were the most common types appeared in the study area. Simulation results are shown in Table 4-3. Four models reported on Table 4-3 show different mass transfer combinations in respect to precipitation or dissolution of several mineral phases that cause chemical composition difference between initial and final water.

According to the simulations, involvement of carbon dioxide enhances the mineral dissolution indicating that dissolution of $CO_2(g)$ take places along the groundwater flow. It is observed that dissolution of gypsum, albite, anorthite, K-feldspar, and illite occurs along the flow path. Especially weathering of gypsum and anorthite provides Ca^{2+} in groundwater, which is the most common ion determining water type of study area. Albite and K-feldspar also can be the source for dissolved alkali metal ions in groundwater. Continuous supplying of Ca²⁺ leads precipitation of calcite, which also increases saturation index of calcite. Precipitation of calcite due to enrichment of Ca²⁺ through dissolution of gypsum can be explained by common ion effect (Jin et al., 2010; Karimi et al., 2019; Zheng et al., 2018). Dissolution of silicates, or albite, K-feldspar and anorthite in this case, indicates the incongruent dissolution liberating cations and producing kaolinite and montmorillonite which are the most stable form in this study area revealed by stability diagram discussed on section 4.2. In case of ion exchange, simulation results show reverse ion exchange which results in excess alkaline earth metal ions over alkali metal ions. Therefore, geochemical evolutions from initial (Ca-HCO₃ type) to final water (mixed type) can be summarized as:

Ca-HCO₃ water + CO2(g)+ Gypsum + Anorthite + Albite + K-feldspar + Illite + CaX₂ + MgX₂→ Mixed type water + Calcite + Kaolinite + Ca-montmorillonite +

NaX

	Model 1	Model 2	Model 3	Model 4	
Phase					
CO ₂ (g)	7.96E+00	4.63E+00	1.59E+01	1.59E+01	
Calcite	-7.96E+00	-4.63E+00	-1.59E+01	-1.59E+01	
Gypsum	6.30E-04	6.50E-04	6.30E-04	6.30E-04	
Albite	0.00E+00	0.00E+00	1.07E+01	1.07E+01	
Anorthite	7.96E+00	4.63E+00	1.32E+01	1.32E+01	
Plagioclase	0.00E+00	0.00E+00	0.00E+00	0.00E+00	
K-feldspar	5.45E-05	0.00E+00	5.45E-05	0.00E+00	
Kaolinite	-7.96E+00	-4.63E+00	0.00E+00	0.00E+00	
Ca- Montmorillonite	-1.14E-04	0.00E+00	-1.59E+01	-1.59E+01	
Illite	2.08E-03	2.10E-03	2.08E-03	2.08E-03	
CaX ₂	2.05E-04	1.49E-04	5.33E+00	5.33E+00	
MgX_2	3.23E-04	3.26E-04	3.23E-04	3.23E-04	
NaX	-1.06E-03	-1.01E-03	-1.07E+01	-1.07E+01	

Table 4-3 Mass transfer for inverse modeling (value in mmol/kgw). Thermodynamic database is from PHREEQC.

4.3.2 Validation of the findings

The results quantify mineral reactions that cause difference of chemical compositions between two points along the groundwater flow path, and verify the findings from conventional geochemical analysis. However, inverse modeling using PHREEQC cannot take into account anthropogenic factors, only for natural processes especially water-rock interaction. So additional study using strontium isotope as a tracer was conducted for solely looking into mineralization controlling groundwater chemistry, and this will be helpful for elaborating the conceptual model describing aquifer system in the study area. Among the natural tracers, strontium isotope was selected, because isotopic ratios of strontium in mineral composing igneous and metamorphic rocks are identical (Shand et al., 2009) and remain unchanged over time. Especially, the study area is mainly composed of granite including Sr-bearing minerals, so strontium isotope analysis is adequate for investigating water-rock interaction solely.

According to the geochemical analysis, extra 8 samples located in the most uncontaminated district were collected for 3 times, and bivariate plots of Sr²⁺ versus selected species are described on Figure 4-8. Firstly, Figure 4-8(a) shows the range of strontium and calcium concentration in additional groundwater sample analyzed for strontium isotope ratio, and Ca²⁺ and Sr²⁺ were correlated. Correlation between two species indicates the fact that Sr^{2+} can be used for tracing sources of Ca^{2+} dissolved in groundwater (Clow et al., 1997). TY-7 was depleted than any other samples, and TY-8 was the most enriched (Fig.4-8a). Figure 4-8(b) and (c) show relation between Sr^{2+} , nitrate and Cl⁻. Generally, nitrate in groundwater is derived from anthropogenic sources, and Cl⁻ behaving conservatively through the hydrological cycle also can derived from human activities. Therefore, if strontium correlated to those contamination indicators, it implies that Sr-content is effected by anthropogenic factors like chemical fertilizers (Négrel & Petelet-Giraud, 2005). TY-8 show enriched strontium, nitrate, and Cl⁻ concentrations which indicates influence of contamination not only the mineral dissolution processes. Wells with higher concentration of nitrate and Cl⁻, including TY-8, locate near apartment and industrial/research complex, so it is possible that groundwater quality exposure to pollutants.

Figure 4-9(a) shows spatial distribution of isotopic ratios. Strontium isotopic ratios range from 0.715094 to 0.717137 with average of 0.715979 \pm 0.000614 for groundwater samples, showing very small variation. In case of surface water, isotopic ratio is 0.715300, which is less radiogenic than those of groundwater samples, except for TY-2. According to the Kim et al. (2000), isotopic ratios of two-mica granite and quartz porphyry, which are main rocks forming Daejeon city, from same study site were 0.71981 and 0.71362, respectively. Range of ⁸⁷Sr/⁸⁶Sr for groundwater samples are in the similar range of two rock samples, dissolved ions like Ca²⁺ and Sr²⁺ can be originated from dissolution of granites (Fig.4-9b). In accordance with ⁸⁷Sr/⁸⁶Sr and 1/Sr, end-members were defined on Figure 4-9(b): (A) TY-6 with high ratio of 1/Sr and most radiogenic sample, (B) surface water (SW) with high ratio of 1/Sr and less radiogenic sample, and (C) TY-8 with low ratio of 1/Sr and less radiogenic sample. But the lack of direct linear relationship between whole samples demonstrates that the existence of multi end-members in the aquifer system (Negrel et al., 2003).

Samples plotted near zone A show more radiogenic and high 1/Sr ratio than others, implying influence by K-bearing silicate minerals like K-feldspar and biotite (Clow et al., 1997; Santoni et al., 2016). Most of the samples on alluvium area and residential/industrial area are clustered on zone B. The selected end-member, TY-8, is more effected by anthropogenic contaminants derived from surface than any other samples, therefore clustered samples near zone B reflect the possibility of contamination from human activities. Also zone B is less radiogenic with low 1/Sr than zone A, representing less-radiogenic and Sr-bearing minerals like anorthite and plagioclase (Clow et al., 1997) or effect of carbonate dissolution such as calcite that is frequently detected as a form of fracture filling mineral in this study area (J. Hwang, 2013). Though the isotopic ratios in groundwater showed very small range, but spatial distribution of ⁸⁷Sr/⁸⁶Sr reflects the bedrock type of sampling points somehow. Furthermore, strontium isotopic ratios verify the findings from geochemical analysis and results from mass transfer simulation: groundwater chemistry in Daejeon city is mainly controlled by silicate mineral weathering with a little of carbonate like calcite.

Figure 4-9 Relation between Sr²⁺, Ca²⁺, NO₃⁻, and Cl⁻

Figure 4-10 Strontium isotopic ratios: (a) spatial distribution of strontium isotope ratio with geological condition, and (b) ⁸⁷Sr/⁸⁶Sr versus 1/Sr distribution in groundwater and surface water (SW)

4.3.3 Conceptual model of hydro geochemical system

Conceptual model explaining aquifer system of Daejeon city is described in Figure 4-10. Results from mass transfer simulation along the selected flow path, geochemical findings related to natural processes like water-rock interactions, and anthropogenic factors are all depicted on the suggested model. When groundwater is recharged in high elevation area proceeding along the regional flow path, fresh groundwater experiences various reactions that bear different groundwater types.

In respect of natural process that control the geochemistry of study area, major cations that determine water type are derived from dissolution of silicate mineral like anorthite, albite, and feldspars, and after releasing cations into groundwater, those minerals transform into more stable phase, or clay mineral form, like kaolinite or montmorillonite. Also, excessive Ca²⁺ ions supplied from dissolution of gypsum or silicates can lead precipitation of calcite with increasing SI value. Ion exchange also engaged in water evolution. As a result, the recharged fresh type water undergoes active water-rock interactions and turns into mixed type groundwater that is much more complex water type. Geochemical characteristics of Daejeon city also reflect land use patterns. Especially area concentrated with industrial/residential complex, and farmland is effected by human activities and land use rather than lithology. Groundwater contamination indicators like nitrate, Cl⁻ are influencing water quality, and especially nitrate is known to induce health problems (Adimalla, 2020; Marghade, Malpe, Duraisamy, et al., 2021; Subba Rao et al., 2020). Thus, regular water quality monitoring will be needed for sustainable water resource management.

Figure 4-11 Conceptual model of hydro geochemical system of Daejeon city, Korea

5 CONCLUSION

In this study, in order to understand the hydro geochemical processes with evaluating quality contamination factors, multiple approaches both quantitative and qualitative were integrated: conventional geochemical analysis, multivariate statistical analysis, and geochemical modeling. Additionally, validation process for mass transfer simulation and geochemical results was also conducted with strontium isotope, in order to eliminate effect of anthropogenic factors that cannot be taken into consideration in quantifying mineral reactions.

As a result, groundwater in Daejeon city is firstly controlled by reaction between aquifer matrix and groundwater. Representative water types are classified into 2 types: fresh type water and mixed type water. Most of the fresh types are located near mountainous and hilly area, and mixed are near old downtown and low land, especially central part of the study site. So the groundwater evolves from fresh to mixed type water according to the elevation of Daejeon city. Along the groundwater flow path, major geochemistry determining water type in study area is weathering of silicate minerals like anorthite, albite and feldspar, in addition to a little calcite and gypsum dissolution and precipitation. Subsequent to dissolution silicates, formation of clay minerals like kaolinite and montmorillonite serves condition for ion exchange, especially reaction that releasing Ca²⁺ and adsorbing Na⁺ onto aquifer matrix. Groundwater contamination indicators like nitrate, Cl⁻, and K⁺ also affect the groundwater quality, and groundwater chemistry of Daejeon city highly reflects the land use patterns according to the PCA and strontium isotope ratios. The potential groundwater contamination sources are residential, industrial complex, and agricultural practices in this study area.

This study successfully applied various description methods, both qualitative and quantitative approaches, for explaining evolution and origin of groundwater chemistry and characterization of hydro geochemistry of granitic urban area. Additionally, isotope analysis that reflects the properties of geological condition of study area was also applied for validating the quantified results. Consequently, the research remedies the blind spot of existing simulation results, and proposes more sophisticated conceptual model that elucidate hydro geochemistry of aquifer in Daejeon city. Moreover, results can be used as guideline for understanding condition of groundwater of Daejeon city. That means this research can show the way how to manage groundwater quality efficiently and help to explicate what potential changes to geochemistry may occur due to the site specification in Daejeon city.

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국문 초록

가뭄, 홍수 등과 같은 기후 문제가 발생하면서, 지하수 자원에 대한 관심이 증가하고 있다. 특히, 지하수 자원의 경우 수질 특성에 따라 사용 용도가 결 정되기 때문에, 효과적인 자원 활용 및 개발을 위해서는 지하수 수질 특성에 대한 이해가 필수적이다. 지하수 수질은 다양한 지질 매체와의 상호작용, 인 간 활동의 영향 등과 같은 요인에 의해 영향을 받기 때문에, 수질 특성 이해 를 위해서는 구조적인 접근이 요구된다. 따라서 본 연구에서는 다변량 통계 분석 기법과 지화학 모델링 프로그램인 PHREEQC를 결합하여, 국내 지질 특성으로 대표되는 화강암반지역의 대수층의 수리지화학적 특성 평가를 수 행하였다.

연구 지역인 대전광역시는 기반암인 화강암, 변성암과 지하수의 상호작용으 로 인한 특성이 두드러지게 나타나고 있는 것으로 확인 되었다. 대표적으로 알바이트, 아노사이트 등의 사장석 용해가 주요 양이온에 해당하는 칼슘, 소 듐의 기원으로 추정되며, 칼슘의 경우 열극 충전 광물로 존재하는 방해석의 용해로부터 기원했을 것으로 추정된다. 열역학 상 안정도와 지화학 모델링 수행 결과, 사장석의 용해와 카올리나이트 등의 점토 광물의 침전 반응이 대 전 광역시의 수질을 지배한다는 것을 확인하였다. 특성 평가를 바탕으로 연 구 지역의 지하수 흐름에 따른 개념 모델을 수립하였으며, 지역적 규모로 추 가 샘플링을 수행하여 스트론튬 동위원소를 활용해 수립한 개념 모델의 정 확도를 높여 주었다.

본 연구는 대전광역시의 지하수 화학 시스템을 모사하는 개념 모델을 제시 하였다는 데에서 의의가 있으며, 물 관리 차원에서 수질을 효과적으로 모니 터링 하기 위한 기초 자료로 활용될 수 있을 것으로 기대된다.

주요어: 수리 지화학, 다변량 통계 분석, 지화학 모델링, 개념 모델

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