J. Soil Groundw. Environ. Vol. 19(2), p. 7~15, 2014 http://dx.doi.org/10.7857/JSGE.2014.19.2.007

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Chemical Characteristics of Groundwater in Carbonate Rock Areas of Korea

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ABSTRACT

This study was conducted to understand the chemical characteristics of groundwater in carbonate areas of Korea. In this study, data on pH, electric conductivity (EC), Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-} were collected from 97 wells which were installed in various carbonate rock regions of Korea. The pH values ranged from 5.7 to 9.9, and the average value was 7.3. The concentration range showed differences between the maximum value of HCO_3^{-} and the medium to minimum values of Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and K^{+} in the study area. The average value of EC was 374 μS/cm, higher than in granite and gneiss areas, where the value is 176 μS/cm. Most of the groundwater was type Ca-HCO_3, and some was type Mg-HCO_3. The relationship between Ca^{2+}, Cl^{-}, and HCO_3^{-}, respectively, and EC showed relatively significant positive correlations compared to the other dissolved components. However, the determination coefficients for Mg^{2+}, Na^{+}, SO_4^{2-}, and K^{+} were very low less than 0.2. These results indicate that the source of Ca^{2+} and Mg^{2+} is relatively simple (carbonate dissolution) compared to other sources. The sources of Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-} might be not only water-rock interactions, but also irrigation return flow, because many groundwater wells had been developed for irrigation purposes. Subsequently, the influence of agriculture on groundwater chemistry was evaluated using a cumulative plot of SO_4^{2-}. The threshold value of SO_4^{2-} calculated from the cumulative frequency curve was 29.2 mg/L. Therefore, 12.4% of all the groundwater wells were affected by agricultural activity.

Key words : Groundwater, Chemical composition, Water-rock interaction, Cumulative frequency curve, Anthropogenic factor

1. Introduction

Groundwater is one of the main sources of fresh water in many areas, and is used for drinking, domestic use, irrigation, and industrial purposes. The demand for groundwater is increasing every day because of urbanization and intensive agriculture (Kim et al., 2004; Siebert et al., 2010; Lee, 2011; Moon et al., 2012). In many areas, excessive use of groundwater has induced problems such as contamination, ground subsidence, and depletion of groundwater. The hydrological and environmental impact may be the result of increasing human activities, and studying the evolution of groundwater helps us to better understand the water processes of this area (Pu et al., 2013). Furthermore, preservation and improvement of groundwater quality is important in securing renewable groundwater resources.

In the study area, groundwater is the most important source of water for agriculture and city development. In recent years, excessive use of groundwater for different purposes has led to its deterioration (Kim et al., 2005). There are many factors that influence the chemistry of groundwater, such as geological processes and structures, host rock mineralogy, and rain precipitation chemistry (Andre et al., 2005). The chemical properties of groundwater in carbonate rock areas are influenced by both natural geochemical processes and anthropogenic factors (Jalali, 2006).

The geochemical systems in groundwater in regions dominated by carbonate rocks are dynamic because of continuous water-rock interactions (Back et al., 1966), and because carbonate minerals have relatively fast dissolution and precipitation kinetics (Linda et al., 2013). Thus, groundwater circulating over long distances in carbonates rocks rapidly reaches equilibrium with carbonate minerals

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Received : 2014. 2. 24 Reviewed : 2014. 4. 30 Accepted : 2014. 4. 30
Discussion until : 2014. 6. 30

(Deike, 1990). Generally, groundwater chemistry depends on many factors, including the nature of recharge, hydrologic gradient, residence time of groundwater, effects of human activities, and water-rock interactions (Kumar et al., 2012). As a result, the geochemical processes and hydrogeological implications in carbonate aquifer systems are well known for many sites throughout the world (Rui et al., 2011).

Different studies have been performed in many countries to identify the effect of carbonate rocks on groundwater chemistry. The influence of climate on the chemical composition of ground-water is especially studied in different parts of the world. This type of experiment was done in France and North Africa by summarizing the concentrations of dissolved solids and selected ions in groundwater (Trainer and Heath, 1976). If the obtained data series are compared to similar conditions in different cities in Korea, the groundwater chemistries which were influenced by the dissolution of carbonate rocks and water-rock interactions can be determined. Dissolution is the partial or complete alteration of minerals due to leaching of its components by water, resulting in dissolution of the rock-forming minerals (Yadav and Chakrapani, 2006). Inter-granular porosity and carbonate rock openings which have been dissolved by water serve as groundwater reservoirs and pathways within the carbonate rocks. The saturation of this water is predominated by the carbonate rock minerals (Jhon, 1972).

In Korea, the groundwater in carbonate rock areas dissolves the minerals in the rocks via water-rock interaction, resulting in the significant presence of carbonate mineral ions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}. The presence of other ions such as Cl^{-} and SO_4^{2-} indicates that other factors are also involved in the dissolution of carbonate rocks in the groundwater. However, the results of these studies do not provide any information on the contamination processes of these areas, as all these processes happen as natural or chemical processes. Most studies in recent years were performed on the groundwater chemistry in Korea's coastal areas (Kim et al., 2004, 2005; Lee et al., 2007; Park et al., 2012).

The main objectives of this study are to evaluate groundwater chemistry data obtained from the Rural Groundwater Net, and to investigate the effect of carbonate rock dissolution on groundwater quality.

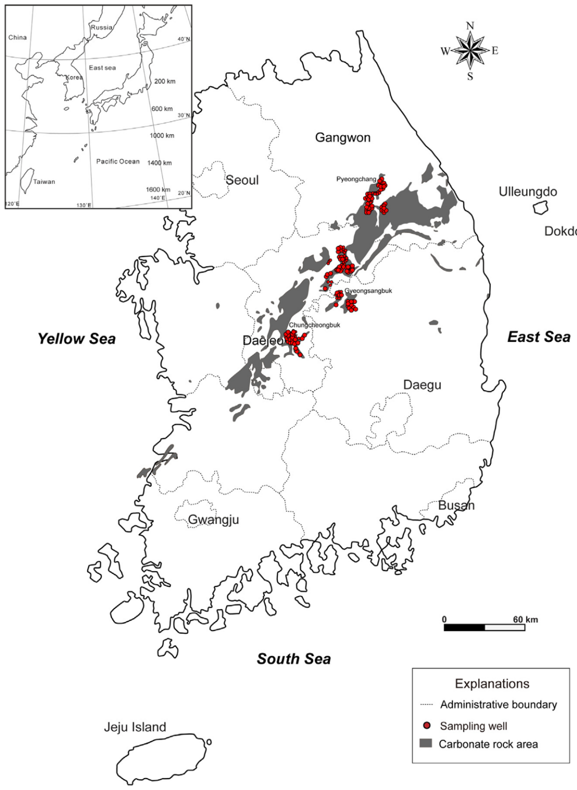

Fig. 1. Well locations in the carbonate rock areas of Korea.

2. Materials and Methods

2.1. Study Area

The study areas distributes in Pyeongchang, Chungcheongbuk, and Gyeongsangbuk of Korea (Fig. 1). Pyeongchang is a county in Gangwon province located approximately 180 km east of Seoul. The area is surrounded by the wide ranging Taebaek Mountains and has a humid continental climate with warm, humid summers, and long, cold winters (Peel et al., 2007). The agricultural activities conducted here use groundwater resources in the area. The most important rivers of Korea, the Han and Nakdong Rivers, both originate in the Taebaek Mountains. Chungcheongbuk is located in the south of Gangwon province, and west of Gyeongsangbuk province, about 60 km east of the city of Daejeon. Our study area is in northern Chungcheongbuk, where the Sobaek Mountains are the main feature. Different types of grain crops are grown in the flat lands of this region. Gyeongsangbuk, the third study area, lies south of Gangwon province and east of Chungcheongbuk province. The northern part of this province is our study area, and is largely surrounded by mountains, with the Taebaek Mountains in the east and the Sobaek Mountains in the west. The climate of this province is hottest during the summer. The rocks of these studied areas mainly consist of carbonate rocks with granite, schist, plagioclase, and metamorphic rocks.

The use and development of groundwater in Korea has been regulated by the Groundwater Law since 1994 (Lee et al., 2007). According to this law, any development of groundwater in excess of the regulated quantity requires permission from the relevant authorities (Lee and Han, 2013). In spite of the strict law, many unofficial groundwater wells are used in the cities and rural areas. We selected groundwater wells in the studied areas on the basis of the geology around the wells. Both deep and shallow groundwater wells were selected.

2.2. General Geology

The geology of the Korean peninsula consists mainly of granite, gneiss, schist, limestone, and metamorphic sedimentary rocks, which formed during the pre-Cambrian to Cenozoic eras (Lee et al., 2007). This is a mountainous region extending south-southeast from the northeastern part of mainland China. Granites and gneisses cover about 60% Korea’s surface, excluding lava flow areas and carbonate-dominated rock areas. There are two major mountain ranges in our study area, the Taebaek Mountains and Sobaek Mountains. The region also contains many tectonic provinces and massifs from north to south. These massifs consist primarily of high-grade gneisses and schists (Ree et al., 1996).

The stratigraphic unit of Gangwon province and its nearby areas is Precambrian gneiss intruded by Jurassic granite, and the rock layers are covered by alluvium. The weathered gneiss has a secondary permeability and is hydraulically connected to the Quaternary deposits (Lee and Lee, 2000). The stratigraphic units in the other two provinces are more or less similar to the Gangwon area, containing Jurassic Daebo granite, Precambrian banded gneiss, Cretaceous biotite granite, and Quaternary alluvium with an abundance of limestone (Hyun et al., 2008).

The geology of the studied area is mainly dominated by carbonate rocks. Some igneous and metamorphic rocks distribute among these carbonate rocks (Fig. 1). In carbonate areas, groundwater chemistry is influenced by chemical weathering of carbonate rocks. Carbonate minerals react quite readily with most groundwater and play an important role in the evolution of groundwater (Allen and Suchy, 2002).

2.3. Hydrogeological Setting

The regional climate of this study area is characterized by seasonal monsoon changes. The annual precipitation indicates the variation of seasonal change. Generally, about 90% of the precipitation takes place from June to September, during the wet season. The snows and ices of both the Taebaek and Sobaek Mountains accumulate at high altitudes during the winter season and begin to melt in the spring, through the summer. This meltwater is a permanent source of streams and watershed for this area. The Han and Nakdong Rivers are the most important and permanent waterbeds formed by rainfall and ice-snow meltwater in this region.

There are two main types of aquifers in Korea, shallow alluvial and deep bedrock aquifers. The shallow aquifers are composed of unconsolidated sediments are distributed along the main river, with a thickness of 2 to 30 meters (Lee et al., 2007). This type of aquifer is the main source of water for agriculture in many rural areas (Kim et al., 2005). Bedrock aquifers generally contain joints, fractures, and faults formed by tectonic activity and are overlain by a shallow aquifer. For drinking water throughout Korea, it is becoming more important to use the deeper and cleaner uncontaminated water (Lee et al, 2007). Both types of aquifers are found in our study area. In hydrogeological environments, the fracture, porosity, and hydraulic conductivity of rocks can be used for hydrological interpretations as to different pathways of groundwater flow and the objectives of hydrogeological study (Krasny, 2002).

The carbonates rocks dominate the area, along with the adjacent granites, gneisses and biotites, which are influenced by the water-rock interactions with the groundwater. Granite leaching were observed from the presence of very high concentration of fluoride in granite and these concentration decreased gradually because of

Table 1. Statistics of major chemical compositions of the groundwater in carbonate rock areas of Korea (n = 97)

Statistics	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	EC
Min	3.0	2.0	0.8	0.3	0.8	0.9	6.5	117.0
Max	116.0	36.3	63.5	14.4	113.6	88.8	293.1	990.0
Avg	53.8	13.1	8.3	2.9	12.8	18.9	136.2	374.0
S.D	23.6	8.7	11.6	3.2	19.0	15.7	65.7	145.6
C.V	0.44	0.66	1.40	1.09	1.48	0.83	0.48	0.39

Values are expressed in mg/L
S.D = Standard Deviation
C.V = Coefficient of Variation

super saturation of fluorite results sufficient Ca^{2+} ion by dissolution of Ca^{2+} bearing plagioclase (Chae et al., 2006). Because of this, the common dissolved components are featured in this incidence, and there are no unknown components. Therefore, the surrounding rocks of the carbonate rocks areas play an important role in the geochemical processes of these areas.

2.4. Data Collection and Analysis

The data used in this study were obtained from the Rural Groundwater Net, which is one of the largest groundwater websites in Korea (www.groundwater.or.kr). The data concerned with the development, use, water quality, management of groundwater in rural areas are served in the Rural Groundwater Net. In addition, data on pH, electrical conductivity (EC), and chemical compositions (Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}) were collected from this website (Table 1) to evaluate groundwater chemistry of carbonate rock areas in Korea. The geochemical data sets were collected from 97 wells in the carbonate rock rich areas, where the EC, pH, and chemical compositions of groundwater were measured regularly using a multi-probe equipped with a data logger in each groundwater well (Lee et al., 2007; MAF and KRC, 2009). We then analyzed the data using linear regression and other statistical methods. Of statistical methods, threshold values calculated from cumulative frequency curves were used to evaluate the environmental impacts such as seawater intrusion and excessive use of fertilizer (Russo et al. 2001; Park et al. 2002; Knight et al. 2005; Lee and Song, 2007; Tutmez 2009; Park et al., 2012). In this study, threshold values were used to estimate background levels of major dissolved components in groundwater.

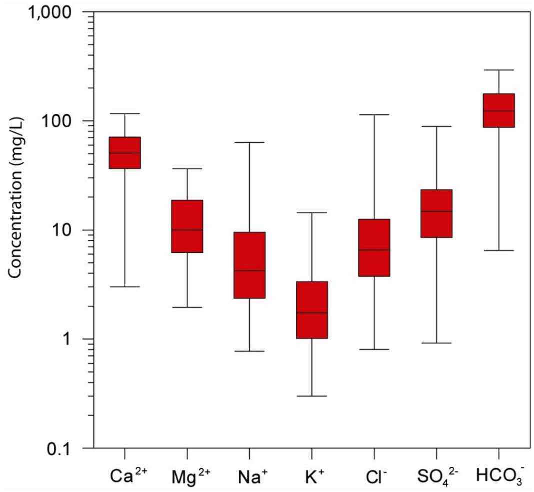

Fig. 2. Box plots of chemical analysis of groundwater.

3. Results and Discussion

3.1. General Chemistry

The chemical composition of the groundwater samples are shown in Table 1. Here the components exist with identical values to describe the chemical characteristics of groundwater and the adjacent carbonate rock areas. The pH value of the groundwater ranged from 5.2 to 9.9, and the average value was 7.3. This pH value is the average value for the wet and dry seasons. This groundwater pH value is neutral to slightly alkaline in nature. Normally, the pH value follows this order of dominance: groundwater > river water > melt water > fresh water > rain water (Pu et al., 2013).

The chemical composition of groundwater is determined by a number of factors, such as rock type and mineralogy of the adjacent areas. Fig. 2 shows the wide range of concentrations of the dissolved components, with medium to high concentrations of Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}, but medium to low concentrations of Mg^{2+} and K^{+}. This

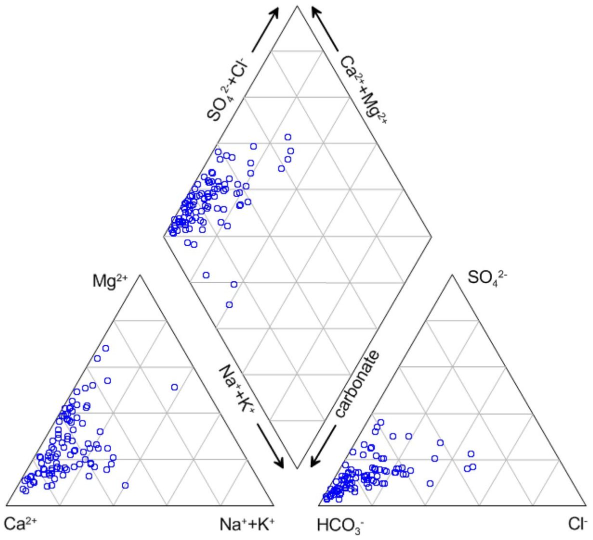

Fig. 3. Chemical composition of the groundwater (n = 97).

indicates that Ca^{2+} and HCO_3^- were mainly affected by simple processes such as water-rock interactions, and K^+, Cl^-, and SO_4^{2-} were affected by human activity or anthropogenic factors. There was a wide range of HCO_3^- values, from 6.5 to 293.1 mg/L. The Ca^{2+} and Mg^{2+} values ranged from 3.0 to 105.6 mg/L and 2 to 36.3 mg/L, respectively, resulting from the water-rock interactions with adjacent carbonate rocks. On the other hand, SO_4^{2-} values ranged from 0.90 to 88.8 mg/L, possibly indicating the presence of sulfide minerals in carbonate rocks or rainfall in these areas. Other sources of SO_4^- are anthropogenic, i.e., the fertilizers and pesticides used in nearby agricultural cultivated areas (Jiang et al., 2009).

Fig. 3 shows the dispersion of the cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) and anions (Cl^-, HCO_3^-, and SO_4^{2-}) in groundwater samples and land use, indicating that these variables could be associated either with carbonate rocks or with human activity. In this diagram, dissolved components were mainly plotted as Ca-HCO_3 or Mg-HCO_3 type, suggesting that the hydrochemistry of groundwater was mainly controlled by water-rock interactions, and SO_4^-, indicates human activity (fertilizers and pesticides), or rainwater mixed in with the groundwater. Generally, Ca^{2+}, Mg^{2+}, and HCO_3^- showed higher concentrations in the groundwater of areas dominated by carbonate rocks, where the water-rock interaction was the primary source of Ca^{2+}, Mg^{2+}, and HCO_3^- in the groundwater. The Mg^{2+} content is

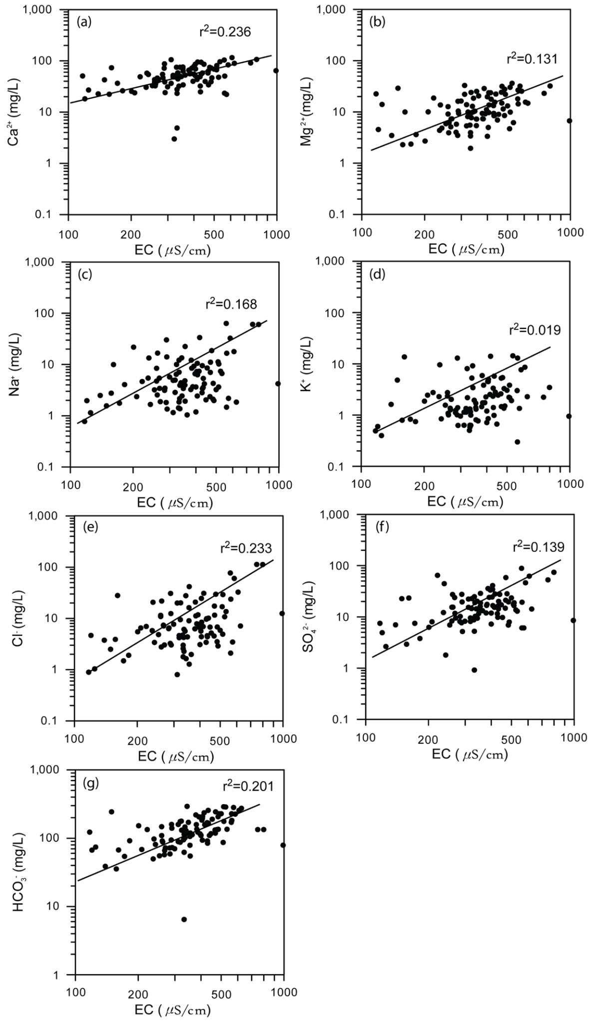

Fig. 4. Relationship between the major chemical components of groundwater with the EC levels.

clearly high in our collected groundwater datasets due to the water-rock interaction in the limestone or dolomite dominated areas (Fig. 3). On the other hand, the relatively high concentrations of Cl^- and SO_4^{2-} reflect some anthropogenic factors in the groundwater.

The major chemical components of groundwater have been used to identify the groundwater chemistry of the surrounding areas. Fig. 4 shows the relationship between the major concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and HCO_3^- with respect to EC. These major components were plotted to identify the effects of the groundwater in the study area. Both anions and cations take part in ion exchange processes. Clays are particularly effective in adsorbing cations because their surfaces are consistently

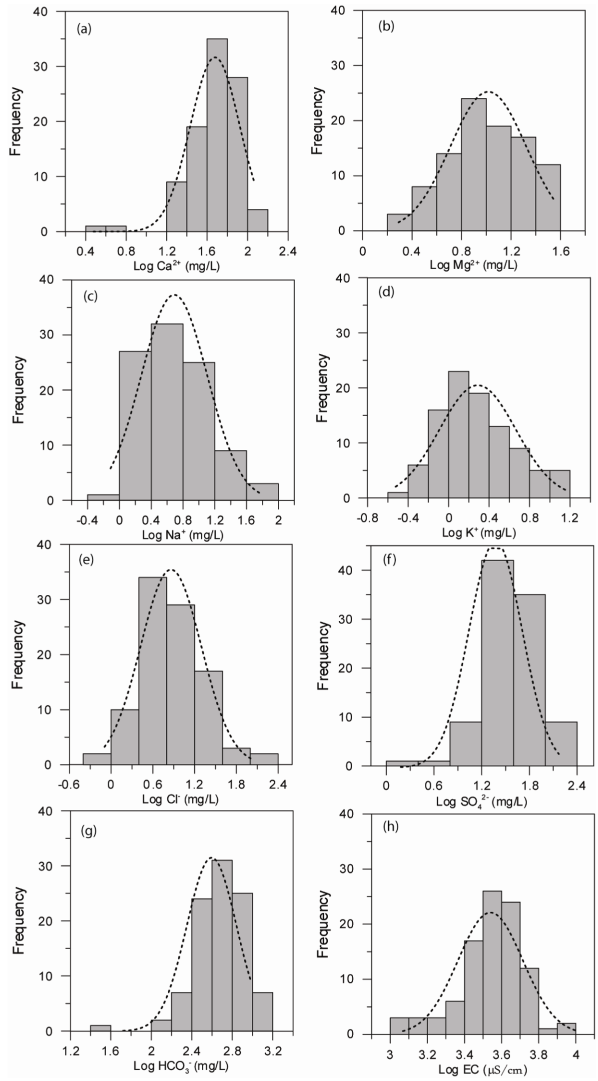

Fig. 5. Distributions of the concentrations of major components.

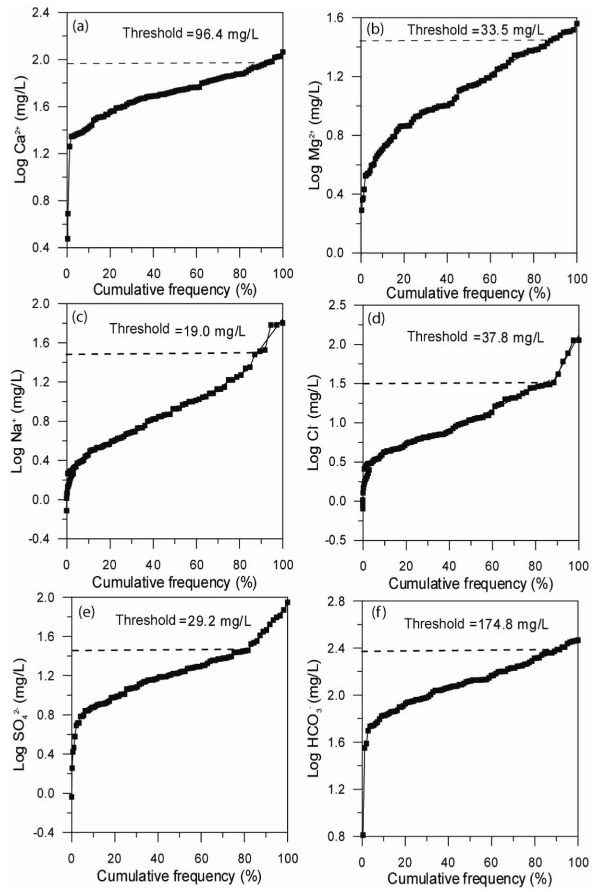

Fig. 6. Cumulative frequency plots for major dissolved components of the groundwater. The threshold values are calculated from intersection point of two linear regression lines of low and high concentration levels.

negatively charged. These major chemical components showed a positive correlation trend due to groundwater dissolution. Most of the components did not show significant positive correlation with EC, especially, these relationship was more distinct in K^+, which showed the lowest value ($r^2 = 0.019$) suggesting decomposition of organic matter (Fig. 4d). Ca^{2+} and HCO_3^- showed relatively good positive correlation ($r^2 = 0.236$, 0.201, respectively) compared to the other components, indicating that these components are supplied from dissolution of carbonate rocks. In addition, Cl^- showed the relatively high value ($r^2 =$ 0.233) because of influence of various anthropogenic factors (Fig. 4e). In this study, sources of Cl were not revealed caused by the limited information for environment around wells.

The concentrations of dissolved components showed similar variation, with low ranges or normal distributions reflected in the dissolution of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, and EC (Fig. 5). One or two sources here are involved in chemical dissolution via water-rock interaction of carbonate rocks and rainfall, or interaction of irrigation water with carbonate rocks through groundwater. Generally, all the dissolved components show a good log normal distribution, suggesting very low effects in this area.

3.2. Cumulative Frequency Curves and Threshold Values

The effects of rainfall, evaporates, and water-rock interactions are indicated by the cumulative frequency curves for dissolved components (Fig. 6). There is the impact of sea water intrusion, TDS, EC, and the amount of dissolved components, with huge differences between seawater and groundwater. However, anthropogenic factors can be vital indicators in the cumulative frequency curves. The threshold values were not showed significantly in cumulative frequency curves of Ca^{2+}, Mg^{2+}, and HCO_3^- (Figs. 6a, b, and f) . These results are attributed to dissolution of carbonate minerals in the study area. However, the threshold values were observed distinctly in cumulative frequency curves of Na^+, Cl^-, and SO_4^{2-} (Figs. 6c, d, and e), indicating the influence of anthropogenic factors. In particular, SO_4^{2-} is released by fertilizer and pesticides applications used in the agricultural fields. A large part of the study areas dominated by carbonate rocks are covered by agricultural fields compared to other areas in South Korea. Fertilizers and pesticides are easily washed out by rainfall or other water and mixed with the groundwater in this area, and as a result, is reflected in the threshold value of SO_4^{2-} (29.2 mg/L) calculated from the frequency curve. Usually, NO_3^- data are used for identifying fertilizers and pesticides application of agricultural influences. Because of the lack of NO_3^- data, the SO_4^{2-} values are used to infer the effects of anthropogenic factors in this study.

3.3. Water-rock Interaction

Associated components indicate the influence of sources of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and HCO_3^- (Fig. 7). Here all the dissolved components are generally abundant in nature, but Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-} are derived from different sources such as carbonate minerals and pyrite dissolution. These are generally abundant in areas dominated by carbonate rocks. The dissolved components are usually generated by the redox conditions of carbonate and pyrites. Ca^{2+} and HCO_3^- are distributed widely through a 1 : 1 line which is influenced by calcite mineral dissolution in the carbonate rock areas (Fig. 7a). The dissolved component is $Ca^{2+}/Na^+ > 1$, indicating Ca^{2+} derived from carbonate minerals, and $Ca^{2+}/Na^+ < 1$ implies concentrations from silicate minerals such as plagioclases (Fig. 7b). The second abundance of carbonate minerals are from calcite and dolomite through the 1 : 1 line (Fig. 7c). Finally, Ca^{2+}, Mg^{2+}, and SO_4^{2-} show the mixed influence of carbonate and pyrite minerals, and abundant distributions of dissolved components (Fig. 7d), but conversely, water-rock interactions of carbonate dissolution supplied by other sources. In addition to these two factors, other influences include rainfall, and fertilizer and pesticides, which are used in the agricultural areas.

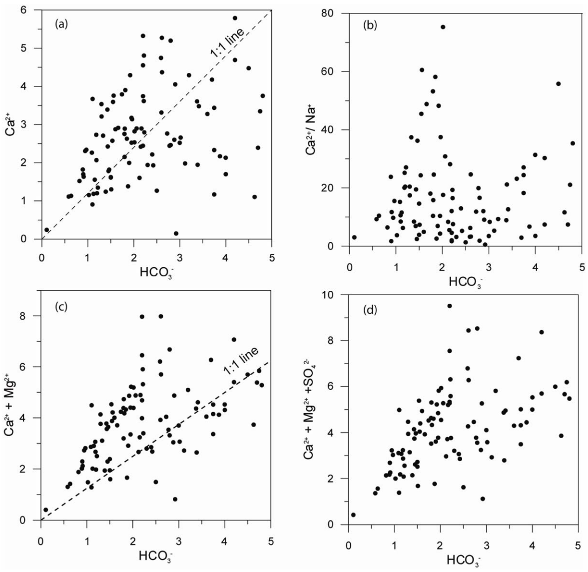

Fig. 7. Distributions of dissolved components.

4. Conclusions

The analysis of groundwater quality reveals that most of the groundwater was type Ca-HCO_3, and some was type Mg-HCO_3. The distribution of ionic concentrations shows a positive trend with wide and narrow ranges of Ca^{2+} and Mg^{2+} with EC, and that the sources of Ca^{2+} and Mg^{2+} were relatively simple, from carbonate dissolution. The leaching effect of surrounding rocks such as granite, gneiss, and biotite releases Ca^{2+} ions from the plagioclase minerals. The groundwater chemistry is influenced by the abundance of carbonates and the adjacent rocks.

As a result, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and HCO_3^- could be supplied by water-rock interactions, and by irrigation return flow and sewage due to the presence of many wells that are used for irrigation purposes. The groundwater in these wells can easily interact with the carbonate rocks. This is concluded from the ionic composition of dissolved components in the groundwater.

Various trends of these dissolved components strongly indicate the dissolution of carbonate rocks and the water-rock interaction that are influenced by the chemical characteristics of groundwater in these carbonate rock areas.

One of the most common known materials released by fertilizer and pesticide applications in the agricultural fields of these carbonate rocks areas is SO_4^{2-}. In this study, most of the wells were established for agricultural purposes, and frequently used for irrigation. This agricultural activity influences groundwater by the inflow and outflow of water. The cumulative plot of all dissolved components and SO_4^{2-} indicates the variation of water-rock interaction and anthropogenic influence. The threshold value of SO_4^{2-} calculated from the cumulative frequency curve was 29.2 mg/L, indicating the anthropogenic effect of agriculture. Therefore, 12.4% of the total groundwater was affected by agricultural activity in the carbonate rock areas of Korea.

Acknowledgements

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (No. 2012-0002628). Special thank is also given to Dr. Mostafa Redwan at Sohag University whose comments and suggestions have significantly contributed to the improvement of the first manuscript. In addition, we would like to thank three anonymous reviewers for their helpful comments.

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