한국지하수토양환경학회 춘계학술발표회
2005년 4월 14~15일 공 주 대 학 교

Water chemistry controlled by the drainage basins: Case study in the Han River, Korea

류종식[1] · 이광식[1] · 신형선[1] · 안규홍[2] · 장호완[3]
*[1]한국기초과학지원연구원 * [2]한국과학기술연구원 * [3]서울대학교 지구환경과학부*
jsryu@kbsi.re.kr

요 약 문

To evaluate the main hydrogeochemical characteristics, river waters are investigated using elemental and isotopic compositions in South Korea. In this area, the chemical compositions are mostly classified into three groups; Ca^{2+}-HCO_3^- type, Ca^{2+}-Cl^--NO_3^- type and Ca^{2+}-HCO_3^--Cl^--NO_3^- type. These types are affected by two major factors: water-rock interaction and anthropogenic inputs such as sewage and fertilizers. Based on the values of $\delta^{18}O$ and δD, most of waters are originated from precipitation except two samples contaminated.

The lithology and geography of basins mainly control the water chemistry. Elemental and isotopic compositions show that water chemistry are mainly controlled by three end members, especially by carbonate dissolution, and suggest that anthropogenic input affect the water chemistry. Also, three weathering sources are identified: silicates, dolomite and limestone.

key word : Water-rock interaction, Anthropogenic input, Carbonate dissolution, Water chemistry.

1. Introduction

To investigate the effect of subsurface weathering on the water chemistry, one of tributaries, the Song River, is selected in the upper reach of the South Han River. The upper and middle reaches of the Song River catchment are dominated by Jurassic granites and sedimentary rocks, and Paleozoic sedimentary rocks (sandstones, shales, sand shales and siltstones). While in the lower reaches are mainly Paleozoic sedimentary rocks (limestones, coal-bearing formations, dolomitic limestones, shales and sand shales) (Data from the Korea Institute of Geoscience and Mineral Resources, "http://geoinfo.kigam.re.kr").

The purpose of this study is to examine the chemical and isotopic compositions in the natural waters to determine processes and factors controlling water chemistry.

2. Results and discussion

The pH value showing downstream enrichment reflects the importance of weathering of carbonates in the watershed. However, TDS values varying from 17.1 to 272.8 mg/l seem to be affected by anthropogenic inputs such as fertilizer rather than weathering of carbonates.

Average total cation concentrations (TZ^+) were 1.79 meq/l (0.16 to 4.26 meq/l). The average TZ^+ values of waters flowing through carbonates and affected by anthropogenic inputs are higher than that of the major world rivers (TZ^+ = 1.25 meq/l; Meybeck, 1981).

For cations, calcium is the dominant ion for the majority of the samples (0.03 to 1.28 mmol/l). The second major cation is Na^++K^+, and its average concentration is 0.20 mmol/l. However, for anions waters are divided into three groups: HCO_3^--dominant type, Cl^-+NO_3^--dominant type and mixed type. The Piper diagram shows that there are three different water types: Ca^{2+}-HCO_3^- type, Ca^{2+}-Cl^--NO_3^- type and Ca^{2+}-HCO_3^--Cl^--NO_3^- type.

On a TDS vs. $Na^+/(Na^++Ca^{2+})$ diagram (Gibbs, 1970), waters could be divided into two major groups: one in the rock dominance field and the other in the precipitation dominance field. Further, waters in the former can be classified into two groups by $Na^+/(Na^++Ca^{2+})$ ratio; one having low $Na^+/(Na^++Ca^{2+})$ ratio and the other having moderate $Na^+/(Na^++Ca^{2+})$ ratio. In general, the concentration of Na^+ in rainwater is greater than that of Ca^{2+}, so that the $Na^+/(Na^++Ca^{2+})$ ratio approaches unity. Therefore, these results indicate that the major mechanism to control the water chemistry is weathering of the carbonates, and that minor mechanisms are atmospheric input and/or anthropogenic input.

Compared to the Global Meteoric Water Line (GMWL, $\delta D = 8*\delta^{18}O + 10$; Craig, 1961), waters align fairly well along the GMWL. However, two groundwater samples have enriched isotopic compositions one collected at limestone basin, the other collected at granite basin. This indicates that the former was affected by different water such as water saturated with carbonates by water-rock interaction, and that the latter was affected by irrigation that causes evapotranspiration and hence high $\delta^{18}O$ and NO_3 level (Vengosh and others 2002). Also, one surface water sample has a little depleted isotopic composition and enriched Cl level. This fact also reveals that sewage water having low $\delta^{18}O$ and high Cl level may play role in the water chemistry.

For carbon isotopes, waters show a positive correlation between pH and HCO_3^-, and between $\delta^{13}C_{DIC}$ and Calcite saturation index. Even though the dissolution products of carbonates could be the dominant source of dissolved inorganic carbon (DIC), carbonate dissolution could not be the only factor controlling water chemistry. However, values of $\delta^{13}C_{DIC}$ do not show a meaningful correlation with pCO_2 and NO_3^-. One groundwater sample and one spring water sample show very low $\delta^{13}C_{DIC}$ value. It reveals that respiration of organic matters and/or anthropogenic input such as fertilizers may affect the water chemistry. In order to understand possible relationship between $\delta^{13}C_{DIC}$ and NO_3^-, more detailed investigations are needed.

The strontium isotopic ratios show that there are the silicate, dolomite and limestone sources, and two mixing trends between these three end members. Also, data distributions suggest that both weathering of carbonates and silicates contribute Sr to the waters, respectively resulting in high and low Sr/Na ratios. However, two samples have high Sr/Na ratio and $^{87}Sr/^{86}Sr$, indicating that anthropogenic input affect water chemistry.

The variations $^{87}Sr/^{86}Sr$ against 1/Sr reveals that clearly different end-members exist in waters. For waters, even though there are three end-members (granite, dolomite and limestone), it is seemed that limestone, dolomite and anthropogenic input are major sources.

3. Conclusions

Elemental and isotopic compositions reveal that water chemistry appear to be at first influenced by the geo-hydrologic characteristics of the drainage basins. Contributions of atmospheric input and anthropogenic input are limited, while weathering of surficial rocks, especially carbonates, are importantly affecting the water chemistry in study area. Compared with the drainage basins, waters flowing silicates have near neutral pH, relatively low TDS and major ion concentrations, but relatively high Si concentrations, whereas waters draining sedimentary rocks exhibits the opposite characteristics. Also, anthropogenic inputs such as sewage and fertilizer seem to affect the water chemistry.

Based on the $\delta^{18}O$ and δD of all water samples, it is shown that waters are originated from precipitation. However, water-rock interaction and anthropogenic input make isotopic compositions more enriched in two samples.

Also, for carbon isotope even through water-rock interaction is the major contributor to the water chemistry, the respiration of organic matters and fertilizer seem to influence the water chemistry.

The Sr isotopic compositions, indicating apparent water-rock interaction with different rock types, suggest that even though there are mainly three end members (silicates, dolomite and limestone) contributing to waters, the another factor affecting water chemistry is seemed to be anthropogenic input such as fertilizer and sewage.

4. References

Craig, H (1961) Isotopic variations in meteoric waters. Science 133: 1702-1703

Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 17: 1088-1090

Meybeck M (1981) Pathways of major elements from land to ocean through rivers. In: Martin JM, Burton JD, Eisma D, (Eds.), River Inputs to Ocean Systems. United Nations Press, New York, pp 18-30

Vengosh A, Gill J, Davisson ML, Hudson GB (2002) A multi-isotope (B, Sr, O, H, and C) and age dating (^{3}H-^{3}He and ^{14}C) study of groundwater from Salinas Valley, California: Hydrochemistry, dynamics, and contamination processes. Water Resour Res 38: 1-17

5. Acknowledgements

The authors would like to thank the Green Korea 21 Program of the Korea Institute of Science and Technology for financial support of this work. The authors also thanks to BK21 program, School of Earth and Environmental Sciences, Seoul National University.