

# Application of stoichiometric method in the assessment of groundwater chemistry in a coastal region having complex contaminant sources

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## <요약문>

Groundwater chemistry in a coastal region having complex contaminant sources was investigated. Water analysis data for 197 groundwater samples collected from the uniformly distributed sixty-six wells were used. Chemical analysis results indicate that groundwaters show wide concentration ranges in major inorganic ions, reflecting complex hydrochemical processes of pollutants. Due to the complexity of groundwater chemistry, Results illustrate that thirty five percent of the wells do not fit for drinking based on nitrate and chloride concentration in the study area. the samples were classified into four groups based on Cl and NO<sub>3</sub> concentrations and the processes controlling water chemistry were evaluated based on the reaction stoichiometry. The results explained the importance of mineral weathering, anthropogenic activities (nitrification and oxidation of organic matters), and Cl-salt inputs (seawater, deicer, NaCl, etc.) on groundwater chemistry. It was revealed that mineral dissolution is the major process controlling the water chemistry of the low Cl and NO<sub>3</sub> group (Group 1). Groundwaters high in NO<sub>3</sub> (Groups 2 and 4) are acidic in nature, and their chemistry is largely influenced by nitrification, oxidation of organic matters and mineral dissolution. In the case of chloride rich waters (Group 3), groundwater chemistry is highly influenced by mineral weathering and seawater intrusion associated with cation-exchange reactions.

**Key words** : Coastal aquifer, anthropogenic contamination, seawater intrusion, mineral weathering, stoichiometric analysis

## 1. Introduction

Geochemical studies on groundwaters in the coastal aquifer are a major concern due to seawater intrusion by over abstraction and anthropogenic contamination (Zilberbrand and others, 2001; Cardona

and others, 2004). In Korea, especially in the coastal region, groundwater has been contaminated by saline water intrusion and anthropogenic activities. In the present study, a detailed geochemical investigation was carried out to identify the groundwater contamination processes using a stoichiometric approach in Kunsan area.

Kunsan City is located in the western coast of the Korean Peninsula and has an area of 372 km<sup>2</sup>. The area has complicated land use characteristics, mainly consisting of agricultural, urban/residential, and forest areas. The alluvium was formed under the inter-tidal environment and occupies the most of Kunsan area (>70%). For this study, 197 groundwater samples were collected from 66 wells during March 2002, August 2002, and February 2003. Electrical conductivity (EC), pH, dissolved oxygen (DO), and temperature were measured directly in the field. Major ions, NO<sub>3</sub> and dissolved silica were analysed in the lab.

## 2. Results and discussion

Chemical analysis results indicate that about 35 % of the wells exceed the Korean Drinking Water standard (DWL) based on nitrate and chloride concentrations (44.3 mg/l, 250 mg/l). Because of the complexity in water chemistry, groundwater samples were classified into four groups based on the concentrations of Cl and NO<sub>3</sub> (Fig. 1a), which represent the influences by saline waters and anthropogenic activities, respectively (Cardona and others, 2004). Groundwaters in Groups 2 and 4 show high nitrate concentration due to the effect of anthropogenic activity, especially oxidation of ammonium and/or organic matter. The plot of total cation ( $\Sigma$  cation) versus chloride indicates that many of the Group 3 waters are plotted along the seawater mixing line (Fig. 1b) and explain the saline water influences. Dissolution of minerals is the most important chemical process in Group 1 samples (Fig. 1c). Fig. 1c shows that only Group 1 samples are plotted most closely to the 1:1 mineral dissolution line (Kim 2003), and implies that dissolution of minerals is the most important chemical process for Group 1. The stoichiometric relationship for mineral weathering in Figs. 1c and d is used to explain the contribution of Cl-salt input, nitrification, and mineral weathering. After the corrections made for the effects of anthropogenic activities and seawater intrusion (Figs. 1e, f), the results show that these  $\Sigma$  cation corrections make the relationships more linear with respect to alkalinity, which indicates that the water chemistry can be mostly explained by Cl-salt input, nitrification, and mineral weathering. Based on the stoichiometric analysis, ' $\Sigma$  cation - Cl' can be referred as the total cation increased by mineral dissolution. Table 1 shows that the mineral weathering contribution is most significant in the Group 3 water due to the intruded seawaters that have resided in the geologic media for a longer time. However, the relative influence of mineral weathering is most significant in the Groups 1 and 2, which show the lower ionic strengths. Based on the stoichiometric analysis, the relative contributions of nitrification and aerobic decomposition of organic matters to the total nitrate concentrations were estimated (Table 1). The results show that nitrate contributions from the organic matter seem to be somewhat greater in Groups 2 and 4 samples. In contrast, nitrification is likely to be the dominant nitrate supplying process in the low nitrate groups (Groups 1 and 3).

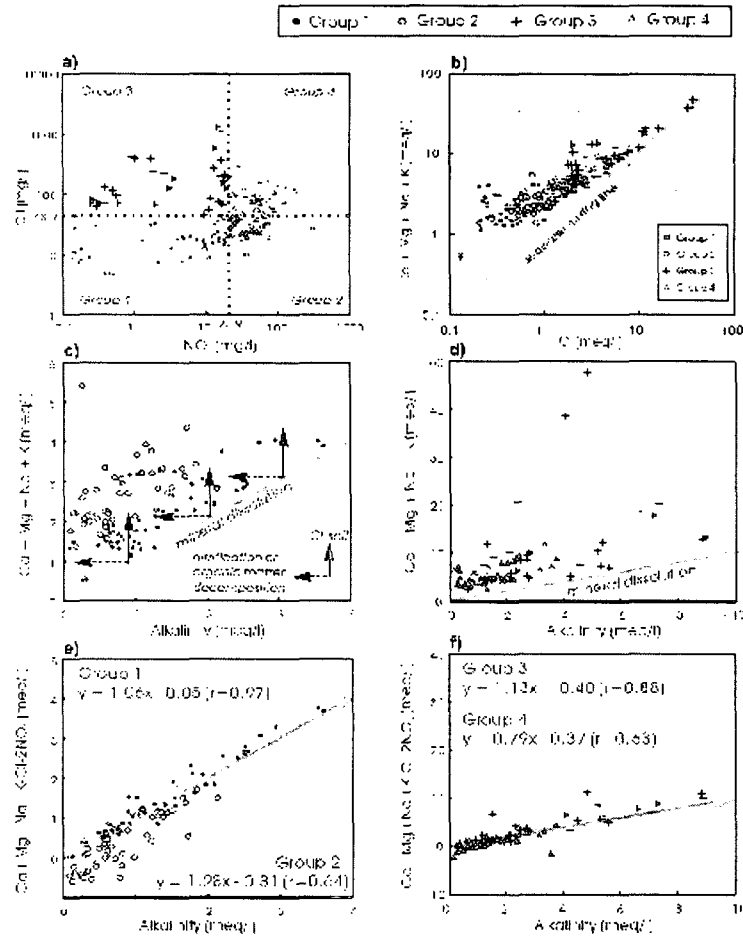


Fig.1. Groundwater classification and geochemical process in Kunsan city, Korea

Table 1. Calculation results for the contributions of various chemical processes to the concentrations of total cation and nitrate. Units are meq/l and the numbers in the parentheses represent the relative contributions for the total concentration.

	Total Cation ( $\Sigma$ cation)			Nitrate		
	Cl-salt	Mineral weathering	Total	Nitrification	Oxidation of organic matter	Total
Group 1	0.49±0.28 (25±13%)	1.61±0.83 (75±13%)	2.09±0.90	0.07±0.08 (71±40%)	0.06±0.09 (29±40%)	0.12±0.11
Group 2	0.83±0.25 (33±11%)	1.76±0.61 (67±11%)	2.59±0.69	0.20±0.18 (32±29%)	0.52±0.33 (68±29%)	0.71±0.28
Group 3	5.95±7.53 (50±20%)	4.65±2.97 (50±20%)	10.60±9.16	0.10±0.12 (80±39%)	0.15±0.81 (20±39%)	0.26±0.80
Group 4	2.56±1.36 (48±12%)	2.68±1.02 (52±12%)	5.24±1.82	0.37±0.31 (42±33%)	0.64±0.56 (58±33%)	1.01±0.53

### 3. Conclusion

Groundwater with complex contaminant sources in a coastal area is investigated to identify the natural and anthropogenic the contaminant sources and their contributions to the observed water chemistry. Due to the complexity in water chemistry, groundwater samples were classified into four groups based on Cl and NO<sub>3</sub> concentration, and were analyzed using the reaction stoichiometry. The stoichiometric analysis results reveals that mineral weathering is the most important process controlling the water chemistry of Group 1 samples even though they are low mineralized. Groups 2 and 4 groundwaters having high nitrate concentration are acidic because of the high influences by oxidation of ammonium and organic matters derived from human activities. In the case of chloride rich Group 3, the groundwater chemistry is regulated by mineral weathering and seawater intrusion associated with cation-exchange reactions. This study also suggests that the mass balance approach based on the reaction stoichiometry can be a useful tool for the geochemical assessment of groundwater in the area having complex contamination sources.

#### Acknowledgements

This study was financially supported both by the Saemankeum Environmental Research Center of Kunsan National University and by the Sustainable Water Resources Research Center of the 21st Century Frontier Research Program (# 3-1-1). The authors thank to Seok-Hwi Kim, Seung-Rok Kim, Young-Soo Ha, Ki-Seung Lee, Mi-Seon Baik, Nam-Sin Kim, and Hyun-Jin Kang for their field and lab assistances.

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