

## 서해 연안지역 천부지하수의 수리지구화학 : 연안 대수층의 해수 혼입에 관한 연구

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## Hydrogeochemistry of shallow groundwaters in western coastal area of Korea : A study on seawater mixing in coastal aquifers

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## ABSTRACT

Salinization is an important environmental problem encountered in coastal aquifers. In order to evaluate the salinization problem in the western coastal area of Korea, we have performed a regional hydrochemical study on shallow well groundwaters ( $N=229$ ) collected within 10 km away from the coastline. The concentrations of analyzed solutes are very wide in range, suggesting that the hydrochemistry is controlled by several processes such as water-rock interaction, seawater mixing, and anthropogenic contamination.

Based on the graphical interpretation of cumulative frequency curves for some hydrochemical parameters (esp.,  $\text{Cl}^-$  and  $\text{NO}_3^-$ ), the collected water samples were grouped into two major populations: (1) a background population whose chemistry is predominantly affected by water-rock interaction, and (2) an anomalous population which records the potential influences by either seawater mixing or anthropogenic pollution. The threshold values obtained are 34.7 mg/l for  $\text{Cl}^-$  and 37.2 mg/l for  $\text{NO}_3^-$ . Using these two constituents, groundwaters were further grouped into four water types as follows (the numbers in parenthesis indicate the percentage of

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each type water): (1) type 1 waters (38%) that are relatively poor in Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, which may represent their relatively little contamination due to seawater mixing and anthropogenic pollution; (2) type 2 waters (21%) which are enriched in Cl<sup>-</sup>, indicating the considerable influence by seawater mixing; (3) NO<sub>3</sub><sup>-</sup>-rich, type 3 waters (11%) which record significant anthropogenic pollution; and (4) type 4 waters (30%) enriched in both Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, reflecting the effects of both seawater mixing and anthropogenic contamination. The results of the water type classification correspond well with the grouping on a Piper's diagram. On a Br×10<sup>4</sup> versus Cl molar ratio diagram, most of type 2 waters are also plotted along or near the seawater mixing line. The discriminant analysis of hydrochemical data also shows that the classification of waters into four types are so realistic to adequately reflect the major process(es) proposed for the hydrochemical evolution of each water type. As a tool for evaluating the degree of seawater mixing, we propose a parameter called 'Seawater Mixing Index (S.M.I.)' which is based on the concentrations of Na, Mg, Cl, and SO<sub>4</sub>. All the type 1 and 3 waters have the S.M.I. values smaller than one, while type 2 and type 4 waters mostly have the values greater than 1. In the western coastal area of Korea, more than 21% of shallow groundwaters appear to be more or less affected by salinization process.

**Key Words :** shallow coastal groundwaters, hydrochemistry, seawater mixing, anthropogenic pollution, Seawater Mixing Index (S.M.I.)

## 1. INTRODUCTION

Salinization is the most widespread form of water contamination, especially in coastal aquifers, and is represented by the increases of total dissolved solids (TDS) and some specific chemical constituents (Nadler et al., 1981; Magaritz and Luzier, 1985; Dixon and Chiwell, 1992; Sukhija et al., 1996; Gimenez and Morell, 1997). Potential sources of salinization are diverse, including natural saline groundwater, halite dissolution, seawater intrusion, oil- and gas-field brine, agricultural effluents, and road salts.

Among the salinity sources described above, seawater intrusion is most common and widespread. In many instances, groundwater contamination from seawater intrusion forces

the abandonment of water wells or entire well fields. In general, the intrusion of seawater into coastal aquifer is a natural consequence of the density contrast between fresh water and saline water, as the denser seawater often forms a deep wedge that may extend for several kilometers inland. Tidal action also impacts on saltwater movement and results in the change of freshwater potentiometric surface due to variation in freshwater recharge or discharge (Cooper et al., 1964). However, potentially more serious problem occurs when a coastal aquifer is overdeveloped on a regional scale. The overpumping results in a general lowering of the freshwater potentiometric surface throughout the area and a progressive and extensive invasion of the aquifer by seawater.

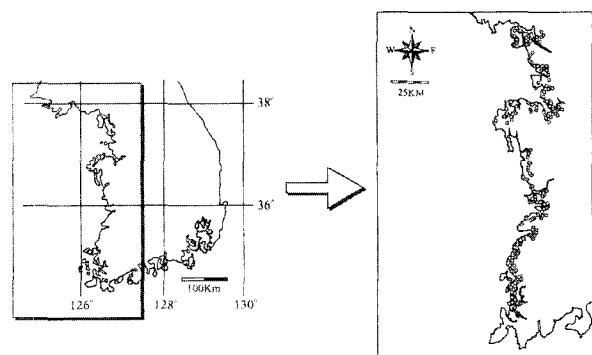
The West (or Yellow) Sea ("Hwanghe") located between China and Korea is a semi-enclosed epicontinental environment. Therefore, the western coast of South Korea is characterized by the macro-tidal regime, with a mean tidal range of up to 6 m. Thus, the potentiality of seawater intrusion into fresh water system is generally high. However, various causes in addition to seawater intrusion probably affect the quality of coastal groundwaters. Rapid industrialization and urbanization in the area possibly cause the anthropogenic contamination of aquifers. Furthermore, the effects of water-rock interaction and/or anthropogenic pollution on groundwater quality are probably significant because the western coastal area mostly covers topographically flat, discharge zones within a groundwater flow regime in a national scale. Therefore, to understand the exact cause of water quality change in a certain region would be a very important task for appropriate management of the coastal groundwaters.

The recharge assessment of fresh water reservoir in coastal aquifers inevitably requires an understanding of the hydraulic and geochemical conditions, including their evolution due to anthropogenic and/or climatic forcing (Mahesha and Nagaraja, 1996). A few hydrogeochemical studies on seawater intrusion in coastal aquifers have been undertaken in South Korea, especially for aquifers in the Cheju Island (Choi and Kim, 1989; Choi et al., 1991; Lee et al., 1997; Jeen et al., 2001). However, these previous studies have only dealt with local groundwaters. In order to understand the general status of groundwater quality in western coastal region of South

Korea, therefore, we have performed a regional hydrogeochemical survey of shallow groundwaters. The acquired hydrochemical dataset has been examined to discriminate the effect of seawater mixing. In this paper, we discuss an integrated approach to discriminate the effects of seawater mixing, anthropogenic contamination, and regional water-rock interaction. We also propose a hydrochemical parameter called "Seawater Mixing Index (S.M.I.)" to quantify the extent of seawater mixing.

## 2. STUDY AREA

The study area is located along the western margin of southern Korean peninsula (Fig. 1). The West (or Yellow) Sea is located to the west of study area. The coastal line is generally curved and forms a 'rias-type' coast especially in the southwestern part of the study area. As the West Sea is a shallow, semi-enclosed epicontinental sea, a tidal effect is generally so high in the coastal zone to form a large tidal effect on surface and possibly ground waters. The spring tidal saline water penetrates up to about 60 km upstream from



**Fig. 1. Sampling sites in the study area.**

the mouth and form a well-defined estuarine environment. The periodic surface water level fluctuation related to the tidal cycle is observed at about 110 km upstream from the mouth (Lee, 1987).

Large amounts of sediments and pollutants are transported to the West Sea via major rivers (e.g., Han, Geum, and Yeongsan rivers) and numerous streams. According to Lee et al. (1992), surface sediments of the western coastal area are several tens meters thick and becomes progressively finer in the shoreward direction, from offshore sand to shoreward silt. Urbanization and industrialization have been intensive ubiquitously in the study area during the past several decades. This land-use change potentially has resulted in contamination of surface and ground waters. Agricultural activities, especially rice cropping, are still pervasive in the study area.

### 3. SAMPLING AND ANALYSIS

For the present study, we have performed a regional hydrogeochemical survey during March to May of 2000. A total of 229 water samples were collected from randomly selected, shallow (mostly <100 m) groundwater wells located within 10 km from the coastline (Fig. 1). The sampling points were chosen to cover uniformly the whole range of western coastal area of South Korea.

The pH, electrical conductivity (EC), and redox potential (Eh) were measured in the field using portable meters. Water samples were collected in polyethylene bottles after filtering with 0.45  $\mu\text{m}$  cellulose membrane

filters. Samples for cation analysis were acidified to pH of <2 by adding ultra-pure nitric acid. Alkalinity was measured using a Gran titration method. Major dissolved ions (Na, K, Ca, Mg, Sr, Cl, Br,  $\text{SO}_4$ ,  $\text{NO}_3$ , and  $\text{SiO}_2$ ) were analyzed by ICP-AES (Perkin Elmer ELAN 3000) and IC (Dionex 120).

Careful quality controls were undertaken for obtaining reliable analytical dataset with an ionic balance error less than 5% (Fritz, 1994). The quality control was achieved by checking carefully the blank samples, calibration standards (NIST 2694a Simulated rainwater, and Perkin Elmer Pure Atomic Spectroscopy Standards), and duplicate or triplicate subsamples. The percentage recovery of ionic species in standard samples was in the range 95-105%.

## 4. RESULTS AND DISCUSSION

### 4.1 General hydrochemistry

#### 4.1.1 Concentrations of major dissolved ions

Whenever seawater mixing is the only source of salt water in a given area, identification of salinization source in an affected well is indicated by an increase in total dissolved solids (TDS) and possibly nearly all kinds of major cations and anions. Table 1 shows the basic statistics of hydrochemical parameters for the analyzed water samples ( $N=229$ ). Very wide ranges and high standard deviations are easily recognized for most parameters. In particular, TDS value has the range between 68 and 29,996 mg/l (mean = 697 mg/l). The ranges of Na and Cl ions are 4.1 to 8,600 mg/l (mean = 145 mg/l) and 3.5 to 16,927 mg/l

**Table 1.** Basic statistics for the quality data of shallow groundwaters (n=229) in western coastal area, Korea.

	pH	mg/l										
		TDS	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	Br	SiO <sub>2</sub>
Min.	5.2	68	4.1	0.4	0.4	0.6	3.5	n.d.	7.6	n.d.	n.d.	n.d.
Max.	8.3	29996	8600	275	1484	1092	16927	1929	704	213	57.1	61
Arith. mean	6.6	697	145	6.2	49	24	283	37	84	39	0.97	28
Median	6.5	244	22	1.9	27	7.4	36	7.8	58	25	0.11	29
S.D.	0.5	2909	848	23	125	107	1622	188	95	41	5.57	12

n.d. = not detected; Arith. mean = arithmetic mean; S.D. = standard deviation

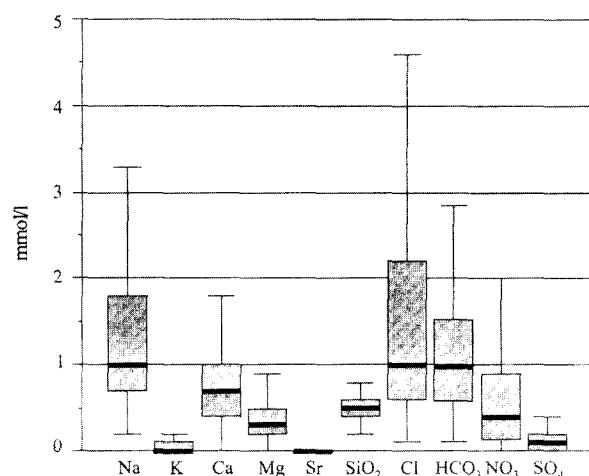
(mean = 283 mg/l), respectively. Such wide ranges possibly indicate that multiple sources and/or complex hydrochemical processes acted to generate the chemical composition.

The analyzed solute concentrations in 229 water samples are graphically shown in Figure 2 as box plots. Of the constituents analyzed, Cl, Na, HCO<sub>3</sub>, Ca, and SiO<sub>2</sub> have the mean concentrations exceeding 0.5 mmoles/l. The dominance of Na and Cl ions in waters

indicate the significant effect of seawater mixing. The considerable amounts of HCO<sub>3</sub> and Ca reflect the contribution from water-rock interaction, while the occurrence of relatively large amount of NO<sub>3</sub> records the considerable anthropogenic pollution. Therefore, we can suggest that the hydrochemistry of shallow groundwaters in the western coastal area are controlled by several processes such as seawater mixing, water—rock interaction, and anthropogenic pollution.

Of the samples analyzed, 53 samples (23%) had the TDS values greater than 400 ppm. Seventeen samples (7.4%) showed the chloride ion concentration exceeding the Korean Drinking Water Quality Standard (250 mg/L). In view of anthropogenic contamination, 78 water samples had significant concentrations of nitrate ( $\geq 45$  ppm).

Sodium and chloride are predominant typically in seawater, while most fresh waters are typically enriched in calcium and bicarbonate (Table 2). To evaluate qualitatively the effect of seawater mixing, we have examined the TDS versus inter-ionic ratios (Ca/Na and HCO<sub>3</sub>/Cl) diagrams (Fig. 3).



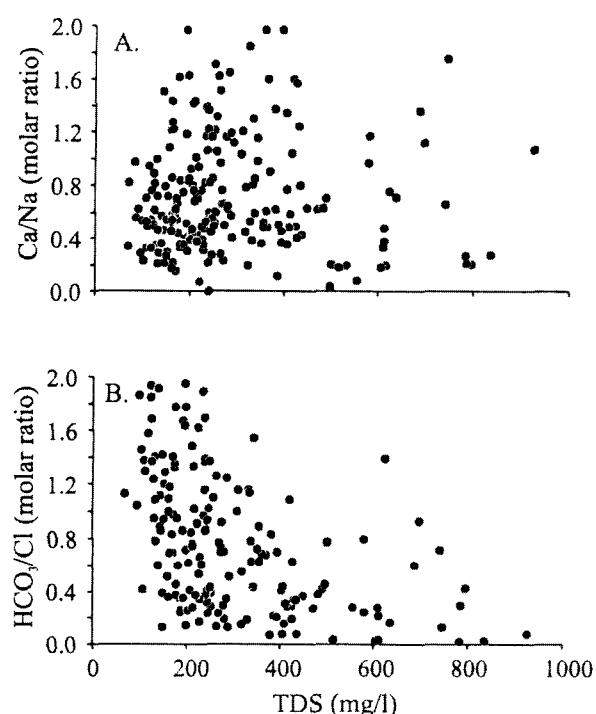
**Fig. 2.** Box plots showing the chemical composition of shallow groundwater in the western coastal area, Korea.

**Table 2. Comparison of the median values of major dissolved constituents in worldwide average surface, ground, and sea waters.**

	Surface water <sup>1)</sup>	Ground water <sup>1)</sup>	Sea water <sup>2)</sup>
Na (mg/l)	6.3	30	10500
K (mg/l)	2.3	3.0	390
Ca (mg/l)	15	50	410
Mg (mg/l)	4.1	7.0	1350
Cl (mg/l)	7.8	20	19000
HCO <sub>3</sub> (mg/l)	58	200	142
SO <sub>4</sub> (mg/l)	3.7	30	2700

<sup>1)</sup> after Turekian (1977)

<sup>2)</sup> after Hem (1985)



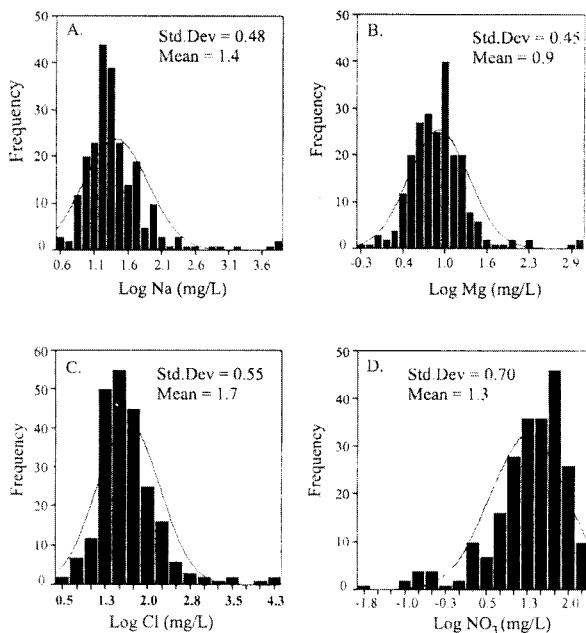
**Fig. 3. Relationships between TDS value and the molar ratios of Ca/Na (in A) and HCO<sub>3</sub>/Cl (in B).**

In the TDS versus HCO<sub>3</sub>/Cl diagram (Fig. 3B), a negative trend between the two variables can be seen. This trend may indicate that high TDS waters are relatively enriched in chloride ion, mainly due to seawater mixing. On the other hand, there is no specific trend in a TDS versus Ca/Na diagram (Fig. 3A), possibly suggesting that Ca/Na ratios in waters are controlled by various factors in addition to seawater mixing.

#### 4.1.2 Density distribution of hydrochemical data

The diversity of natural processes results in complicated geochemistry of a certain material but can be reflected in a set of analytical data. To describe adequately the density distributions found in geochemical data, many mathematical models have been described. Regarding the form of density distributions, the 'normal' and 'log-normal' models are considered to be of great importance in dealing with geochemical data (Shaw, 1961; Sinclair, 1976). In many cases a logarithmic transformation of raw data provides a 'normal' form to the density distributions, in which case the data are said to be 'log-normal'. In such a case, raw data can be dealt with conveniently by applying a substantial number of statistical methods and tests.

Most of the hydrochemical parameters obtained in this study generally showed the 'log-normal' density distributions. Figure 4 shows the 'log-normal' density distributions for Na, Mg, Cl, and NO<sub>3</sub> concentrations. It should be noted that Na and Cl are major components of seawater, while NO<sub>3</sub> is an indicator of anthropogenic pollution. However, the occurrence of an anomalous population as

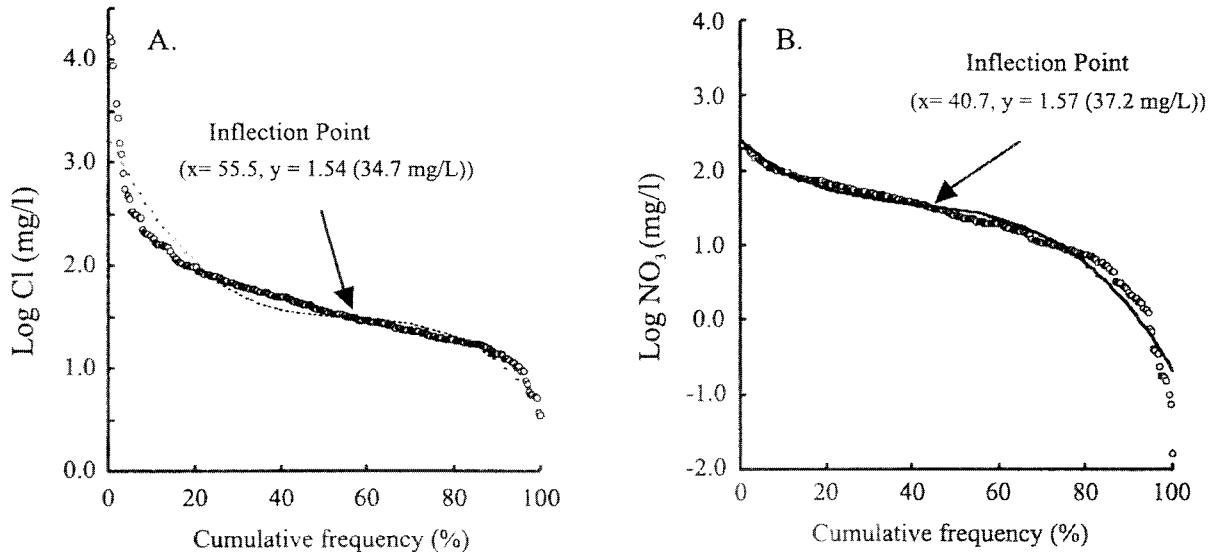


**Fig. 4.** Histograms showing the log-normal distribution of major ions in groundwaters (n=229).

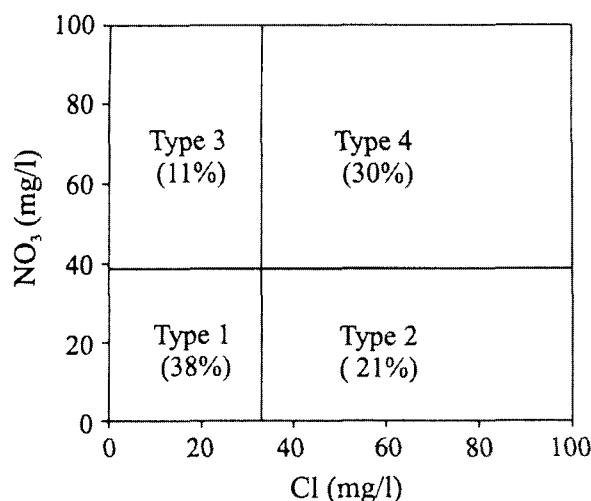
a ‘tail’ in the diagram suggests that the groundwater chemistry is controlled by several intermixed processes such as water-rock interaction (a regional background factor), seawater mixing, and anthropogenic pollution.

#### 4.2 Graphical differentiation of seawater mixing

To determine a threshold value for the differentiation of ‘anomalous population’ from ‘background population’, we used a plot of the cumulative frequency distribution on a log probability paper (Tennant and White, 1959). If the cumulative frequency curve forms an S-shape, the considered geochemical data consist of two ‘log-normal’ populations. The inflection point on the S-shape curve gives an estimate of both the portions of the two populations (background, and anomalous) in the mixture and the threshold value (Lepeltier, 1969;



**Fig. 5.** Cumulative frequency curves for the concentrations of Cl (in A) and NO<sub>3</sub> (in B) in groundwaters. The estimation of inflection points corresponding to the threshold value is based on Sinclair (1974).



**Fig. 6. Four designated groups of groundwaters (n=229) in the western coastal area, Korea, which are classified based on the interpretation of cumulative frequency curves of Cl and NO<sub>3</sub> concentration (after Sinclair, 1974).**

Sinclair, 1974, 1976).

The results of the interpretation of the cumulative frequency curves for two parameters (chloride and nitrate) are shown in Figure 5. The two parameters chosen are considered to reflect the effects of seawater mixing and anthropogenic pollution, respectively. The threshold values obtained are 34.7 mg/l for Cl and 37.2 mg/L for NO<sub>3</sub>. Using the two parameters, the collected waters are divided into two major populations: (1) a background population whose chemistry is largely affected by water-rock interaction, and (2) an anomalous population which reflects their potential influences by seawater mixing and/or anthropogenic pollution.

Using the criteria, shallow groundwaters in western coastal area can be subdivided into

four types as follows (Fig. 6; Numbers in parenthesis indicate the percentage of each type waters): type 1 waters (38%) that are relatively poor in Cl and NO<sub>3</sub>, which may represent their insignificant contamination from seawater mixing and anthropogenic pollution; (2) type 2 waters (21%) which are enriched in Cl, indicating their considerable influence by seawater mixing; (3) NO<sub>3</sub>-rich, type 3 waters (11%) which record sufficient anthropogenic pollution; and (4) type 4 waters (30%) enriched in both Cl and NO<sub>3</sub>, reflecting the effects of both seawater mixing and anthropogenic contamination.

#### 4.3 Hydrochemical evolution

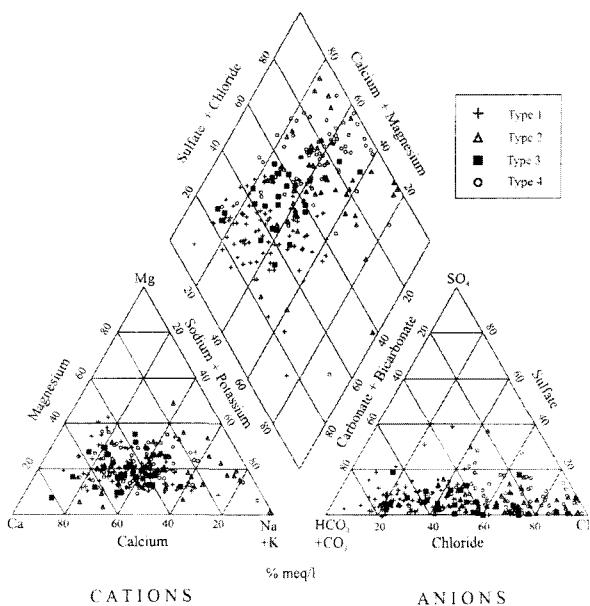
Table 3 summarizes the statistical data for each groundwater type. The TDS values and the concentrations of Na and Cl are typically high in type 2 and type 4 waters. Type 2 and type 4 waters are also characteristically enriched in Mg, SO<sub>4</sub>, and Br, evidencing that they record the influence of seawater mixing. On the other hand, type 1 waters are generally low in the concentrations of most solutes except bicarbonate. Type 3 waters are characterized by relatively low Na, Cl, and SO<sub>4</sub> but high NO<sub>3</sub> concentrations.

Plots of major ion concentrations on a Piper's diagram (Fig. 7) also can be used to distinguish the hydrochemical evolution (and origin) of each water type (Monterey County Flood Control & Water Conservation District, 1989). Type 1 waters are plotted in the field of the Ca-HCO<sub>3</sub> hydrochemical facies, indicating that they were evolved mainly through water-rock interaction in aquifers; type 2 waters represent the Na(-Ca)-Cl facies, reflecting the

**Table 3.** The minimum, maximum, and geometric mean (G.M.) values of hydrochemical data for each groundwater type.

		mg/l									
		TDS	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	Br
Type 1 (n=87)	Min.	68	4	n.d.	4	1	3	n.d.	12	n.d.	n.d.
	Max.	533	91	7	60	20	34	48	300	35	0.25
	G.M.	167	13	1	17	4	17	3	60	8	0.06
Type 2 (n=48)	Min.	161	16	n.d.	n.d.	1	35	1	20	n.d.	n.d.
	Max.	29996	8600	275	1484	1092	16927	1929	655	36	9.50
	G.M.	470	61	4	35	14	128	14	81	6	0.40
Type 3 (n=25)	Min.	150	8	1	11	2	9	n.d.	8	38	0.05
	Max.	429	46	7	77	11	34	33	186	109	0.40
	G.M.	218	18	2	24	6	24	2	43	55	0.09
Type 4 (n=69)	Min.	188	17	1	10	3	37	n.d.	10	38	n.d.
	Max.	6181	1911	88	285	182	2733	357	704	212	9.50
	G.M.	432	46	4	44	14	95	12	52	76	0.20

n.d. = not detected (below the detection limit)

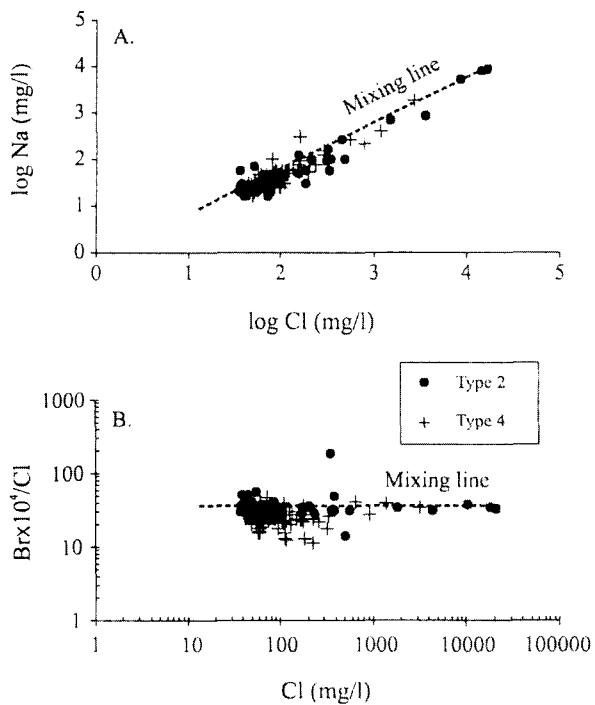


**Fig. 7.** Piper's diagram showing the chemistry of groundwaters.

effect of seawater mixing with potential contribution from cation exchange reactions in aquifers; type 3 waters show the Ca-Cl(-HCO<sub>3</sub>)

facies with enhanced NO<sub>3</sub> concentration; and type 4 waters mainly belong to the Ca-Cl facies. Therefore, the Piper's diagram also indicates that both type 2 and type 4 waters are typically influenced by seawater mixing.

Figure 8 shows the relationships among some hydrochemical parameters that are usually used to distinguish potential seawater mixing. The ideal seawater mixing line also shown in each diagram. If seawater intrudes into a freshwater aquifer, the Na/Cl ratio of the invaded groundwaters are progressively changed along the mixing line (Custodio, 1987). The Br×10<sup>3</sup>/Cl versus Cl diagram is also used as the best geochemical tool for identifying the seawater mixing, owing to the conservative nature of Br and Cl. The Br/Cl ratio is also very helpful to differentiate between seawater and halite-dissolution brine (Richter et al., 1993; Whittemore, 1988). In each diagram, most of the type 2 and type 4



**Fig. 8.** The relationships between Cl concentration and some hydrochemical parameters for type 2 and type 4 groundwaters. Solid line indicates the ideal mixing with seawater.

waters are plotted along or near the seawater mixing line (Fig. 8). This indicates that they records the influence of seawater mixing.

#### 4.4 Geostatistical analysis: re-examination of hydrochemical evolution

In order to re-examine the thoroughness of the hydrogeochemical evolution and origin proposed for each water type, we have performed both factor analysis and discriminant analysis.

The results of one-way ANOVA test (a kind of variance analysis) show that there is statically significant differences between water types (Table 4). Type 1 waters are differentiated from other type waters especially in terms of TDS, Ca, Cl, and NO<sub>3</sub>. Type 3 waters are discriminated in NO<sub>3</sub> concentration from the other type waters. The differentiation between type 2 waters and type 3 waters are obvious in the concentrations of most solutes including Na, Cl, and NO<sub>3</sub>.

**Table 4.** Results of the variance analysis for shallow groundwaters(n=229) in western coastal area, Korea.

	Independent Samples Test (p<0.05);					
	Between Water Types (Sig.(2-tailed))					
	1 vs 2	1 vs 3	1 vs 4	2 vs 3	2 vs 4	3 vs 4
pH	0.17	0.15	0.00	0.23	0.00	0.33
TDS	0.00	0.00	0.00	0.00	0.81	0.00
Na	0.00	0.11	0.00	0.00	0.43	0.00
K	0.00	0.11	0.00	0.00	0.44	0.00
Ca	0.00	0.02	0.00	0.42	0.00	0.00
Mg	0.00	0.12	0.00	0.01	0.07	0.00
Sr	0.00	0.19	0.00	0.04	0.07	0.01
Cl	0.00	0.06	0.00	0.00	0.42	0.00
SO <sub>4</sub>	0.00	0.54	0.00	0.01	0.28	0.09
NO <sub>3</sub>	0.07	0.00	0.00	0.00	0.00	0.00
HCO <sub>3</sub>	0.00	0.35	0.52	0.01	0.00	0.63

**Table 5. Rotated factor loading matrix for type 2 waters.**

Parameter	Factor 1	Factor 2	Communality
Log Ca	0.838	-0.139	0.722
Log Mg	0.922	0.131	0.868
Log K	0.869	0.124	0.771
Log Na	0.936	0.195	0.914
Log Cl	0.959	0.071	0.925
Log HCO <sub>3</sub>	0.663	0.516	0.707
Log NO <sub>3</sub>	-0.012	-0.954	0.910
Log SO <sub>4</sub>	0.830	0.233	0.744
Eigenvalue	5.437	1.124	
Cummulative %	67.96	82.01	

As the variance analysis indicated the significant differences between the water types proposed, we have performed factor analysis (Tables 5 and 6). For type 2 waters, two factors with the eigenvalues greater than 1 were chosen (Table 5). Factor 1 has the high loadings in Cl, Na, and Mg and accounts for 67.9% of the total variance, indicating the significant involvement of seawater components. Factor 2 has a high negative loading in NO<sub>3</sub>, indicating that type 2 waters are free of nitrate contamination. Therefore, we confirm that type 2 waters record the strong effect of seawater mixing. For type 3 waters, on the other hand, three factors showed the eigenvalues greater than 1 (Table

**Table 6. Rotated factor loading matrix for type 3 waters.**

Parameter	Factor 1	Factor 2	Factor 3	Communality
Log Ca	0.863	-0.100	0.174	0.786
Log Mg	0.538	0.133	0.526	0.584
Log K	-0.123	0.853	0.153	0.767
Log Na	-0.130	0.818	-0.130	0.703
Log Cl	0.129	0.669	0.113	0.477
Log HCO <sub>3</sub>	0.925	-0.141	-0.146	0.897
Log NO <sub>3</sub>	-0.020	0.111	0.869	0.768
Log SO <sub>4</sub>	0.572	0.160	-0.500	0.603
Eigenvalue	2.268	1.931	1.386	
Cummulative %	28.35	52.48	69.81	

6). Factor 1 has the high loadings in HCO<sub>3</sub> and Ca. These two ions are known to reflect the contribution of water-rock interaction. Factor 2 has the high loadings in K, Na, and Cl, possibly reflecting the contamination from K fertilizer and/or domestic sewage. Factor 3 characterized by high NO<sub>3</sub> loading also indicates the role of anthropogenic contamination.

The discriminant analysis has been performed to evaluate the reality of the classification of waters into four types (Table 7). The canonical correlations of Function 1 and Function 2 were 0.827 and 0.763, respectively. The Hit Ratio indicating the reality of the classification was also very high

**Table 7. Results of discriminant analysis (N=229, Hit Ratio=86.9%).**

Group	Count	Predicted group membership			
		Type 1	Type 2	Type 3	Type 4
1	87	73(83.9%)	2(2.3%)	12(13.8%)	0(0%)
2	48	6(12.5%)	40(83.3%)	1(2.1%)	1(2.1%)
3	25	0(0%)	0(0%)	25(100%)	0(0%)
4	69	0(0%)	1(1.4%)	7(10.1%)	61(88.4%)

(86.9%), indicating that the results of our grouping into four types are significantly meaningful. Therefore, the chemistry of each type water well explains their distinct hydrochemical process(es) and origin as described above.

#### 4.5 Quantitative estimation of seawater mixing

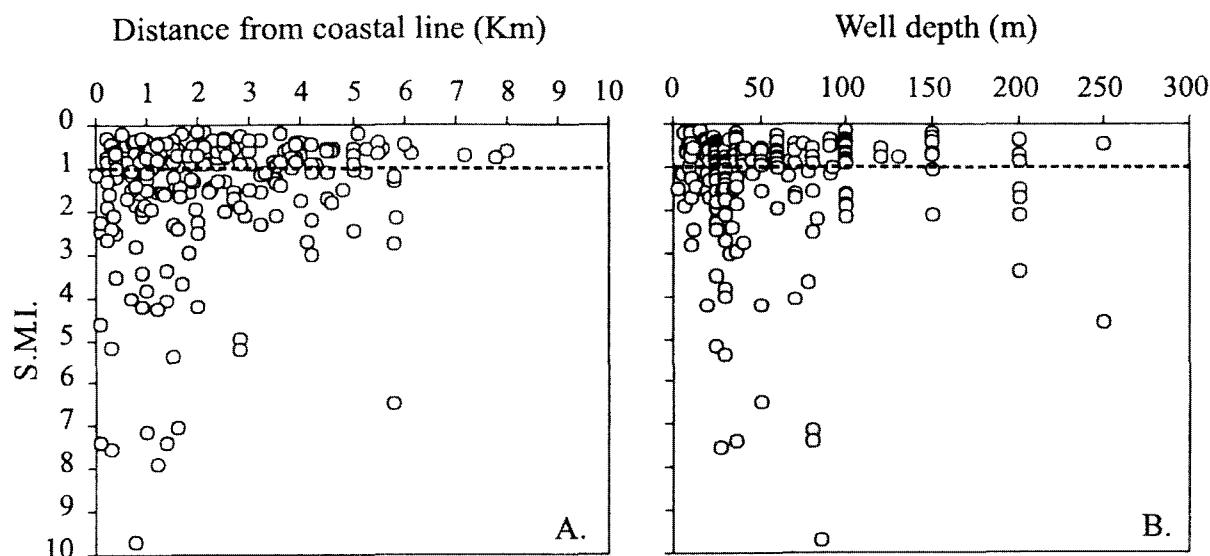
To quantitatively estimate the degree of seawater mixing in a certain water, we propose a parameter called "Seawater Mixing Index (S.M.I.)". This parameter is based on the concentrations of four major constituents in seawater (Na, Cl, Mg, and SO<sub>4</sub>) as follow:

$$\text{S.M.I.} = a \cdot \frac{C_{\text{Na}}}{T_{\text{Na}}} + a \cdot \frac{C_{\text{Mg}}}{C_{\text{Mg}}} + c \cdot \frac{C_{\text{Cl}}}{T_{\text{Cl}}} + d \cdot \frac{C_{\text{SO}_4}}{T_{\text{SO}_4}}$$

where the constants a, b, c, and d denote the relative concentrations of Na, Mg, Cl, and

SO<sub>4</sub> in seawater, respectively ( $a = 0.31$ ,  $b = 0.04$ ,  $c = 0.57$ ,  $d = 0.08$ ); C is the measured concentration in mg/L; and T represents the estimated threshold values of the ions ( $T_{\text{Na}} = 20.1$  mg/L,  $T_{\text{Mg}} = 5.31$  mg/L,  $T_{\text{Cl}} = 34.7$  mg/L,  $T_{\text{SO}_4} = 55.6$  mg/L). If the S.M.I value is larger than 1, the water can be considered to record potential effect of seawater mixing. All the type 1 and type 3 waters have the S.M.I. values below 1, while most of the type 2 and type 4 waters have the values greater than 1. Therefore, at least 117 waters (about 51% of the analyzed samples) belonging to type 2 and type 4 are considered to be more or less affected by seawater mixing.

In order to examine the degree of seawater mixing in terms of the distance from local coastal line and the depth of wells, we have drawn the S.M.I. value versus locality or well depth diagrams (Fig. 9). In Figure 9A, we can see a weak trend of the S.M.I. values



**Fig. 9. Horizontal (in A) and vertical (in B) distribution of the calculated 'Seawater Mixing Index (S.M.I.)'.**

decreasing with increasing distance. Samples with the S.M.I. values greater than 1 are pervasive within the distance up to 6 km away from the coastal line. However, the correlation between the S.M.I. value and well depth is not clear (Fig. 9B). The weak or no trends in Figure 9 indicate that hydrogeologic setting of shallow groundwaters in western coastal area is rather complex and possibly controlled by irregular fracture networks.

## 5. MAJOR CONCLUSIONS

The quality of shallow groundwaters in western coastal area of South Korea seems to be controlled by various causes such as seawater mixing, anthropogenic contamination, and water-rock interaction. The application of an integrated approach consisting of the graphical differentiations and geostatistical analysis for acquired hydrochemical parameters was undertaken in this study in order to differentiate the causes of water chemistry change. Based on the examination of the density distribution of chloride and nitrate concentrations in a total of 229 groundwater samples, the collected water samples were grouped into four types: type 1 waters (38% of the collected samples) which are interpreted to reflect their insignificant influence by seawater mixing and anthropogenic pollution; type 2 waters (21%) enriched in chloride content, whose chemistry is largely influenced by seawater mixing; nitrate-rich, type 3 waters (11%) that is characteristically affected by anthropogenic contamination; and type 4 waters (30%) recording the effects of seawater mixing and

anthropogenic contamination. Type 2 and type 4 waters are also typically enriched in Na, Mg, SO<sub>4</sub>, and Br ions, compared to type 1 and type 3 waters. Both the use of conventional diagrams such as Piper's plot and the geostatistical interpretation of hydrochemical data also supported the reality of the classification of waters into four types.

As an effective tool for the evaluation of seawater mixing in a certain water sample, we proposed a parameter called "Seawater Mixing Index (S.M.I.)" in this study. The samples having the S.M.I. values greater than unity can be considered to reflect the effect of seawater mixing. All the type 1 and type 3 waters had the S.M.I. values smaller than 1, while most of the type 2 and type 4 waters had the values greater than 1. We suggest that about 117 samples (51% of the collected samples) belonging to type 2 and type 4 possibly reflect varying degrees of seawater mixing. However, further studies based on environmental isotopic and hydrogeologic data should be undertaken to ascertain the origin and hydrochemical evolution of groundwaters in the study area.

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