Geosciences Journal
Vol. 11, No. 3, p. 259 − 270, September 2007

Groundwater chemistry and ionic ratios in a western coastal aquifer of Buan, Korea: implication for seawater intrusion

Jin-Yong Lee *Department of Geology, Kangwon National University, Chuncheon 200-701, Korea*
Sung-Ho Song* *Rural Research Institute, Korea Rural Community and Agriculture Corporation, Ansan 425-170, Korea*

ABSTRACT: Seawater intrusion was studied in a monitoring well field, located in western coastal area of Buan, Korea using groundwater chemistry and ionic ratios. Most of the study area is paddy fields apart from 200-2,500 m from the coast. The groundwaters affected by the seawater intrusion featured high levels of Cl and TDS, which are the simplest common indicators for the seawater influence. The TDS showed highly positive correlation with the other major parameters except for nitrate. High levels of NO_3 at some monitoring wells indicated nitrate pollution of groundwaters due to anthropogenic origin such as septic effluents or chemical fertilizers. Based on the piper plot, it was inferred that the groundwater salinization occurred via mixing and cation exchange reaction between two end members (fresh or less affected groundwater and the seawater). Beside of the major chemical compositions, it was demonstrated that ionic ratios would be useful to delineate seawater intrusion and they include HCO_3/Cl, Na/Ca, Ca/Cl, Mg/Cl and Ca/SO_4. Cluster analysis based on these ratios produced an equivalent result to that of using the major chemical compositions. Finally, to differentiate causes of the high salinity in groundwaters between anthropogenic origin (excessive groundwater use) and natural phenomenon (seawater intrusion wedge), consecutive monitoring of groundwater is required for multi-years.

Key words: Seawater intrusion, coastal aquifer, cluster analysis, ionic ratio, Korea

1. INTRODUCTION

Pollution of fresh groundwater due to seawater intrusion has been a public grievance in many coastal areas in Korea (Kim et al., 2003a, b; Kim et al., 2004; Park et al., 2005). Thus protection of the groundwater from the saline water encroachment has a great implication for sustainable agriculture especially in western coastal areas of the country (Lee and Song, 2007). It was reported that effects of seawater mixing with fresh groundwaters were observed even up to about 6 km inland and over 21% of the shallow groundwaters were affected by the salinization process in the western coasts of the country (Park et al., 2002), which was largely attributed to intensive and extensive groundwater pumping in the coastal areas.

Relevant authorities of the country (Ministry of Agriculture and Forestry) have undertaken some investigation and research projects to evaluate status of the seawater intrusion in the coastal areas and to develop reasonable technical approaches mitigating the saline water encroachment. As one of the groundwater monitoring programs in the country, a seawater intrusion monitoring network (SIMN) consisting of 55 monitoring wells in 25 coastal regions has been established since 1998 (Lee and Song, 2007), from which groundwater level, water temperature and electrical conductivity are automatically measured every hour. In earlier than this, a local groundwater monitoring network has been constructed and operated to monitor groundwater levels and electrical conductivities and to evaluate seawater intrusion in Jeju island of Korea because it is mostly dependent on groundwater for water supply (MAF and KARICO, 2003).

In the meanwhile, there have been some methodologies to identify groundwater pollution or salinization by seawater intrusion, which mainly include geophysical surveys, consecutive or intermittent monitoring of groundwater chemistry or both of them (e.g., Jeen et al., 2001; Benkabbour et al., 2004; Sherif et al., 2006; Lee and Song, 2007). Earth (surface) resistivity methods including DC resistivity method and vertical electrical soundings and small-loop electromagnetic survey have been widely applied to delineate seawater intrusion (Hwang et al., 2004; Sherif et al., 2006; Song, 2006). Ionic ratios such as Cl/HCO_3, Cl/Br, and Na/Ca in chemical compositions of groundwaters can be effectively used to differentiate degree of seawater intrusion (Sánchez-Martos et al., 2002; Kim et al., 2003b; El Moujabber et al., 2006). In addition, trace elements and isotopes have been frequently used for the study of saline water intrusion in coastal areas (Vengosh et al., 2002; Murad and Krishnamurthy, 2004).

The objective of this study is to evaluate seawater intrusion in a western coastal area of Buan, Korea using groundwater chemistry data and ionic ratios of them. For this, 15 groundwater monitoring wells were newly installed in the study area, whose distance from the coast ranges between 500 and 1,500 m. Groundwater samplings and subsequent chemical analysis were performed for the monitoring wells.

*Corresponding author: shsong84@hanmail.net or shsong@ekr.or.kr

2. METHODS AND MATERIALS

2.1. Study Site Characteristics

The study site is located in a coastal area of Buan-gun, Jeonbuk, about 200 km south of Seoul, capital of Korea and it is in contact with the West Sea (Yellow Sea) to the west (Fig. 1). There exist some low relief mountains to the other three directions. Most areas in the middle of the study site are paddy fields. Thus some groundwater wells have been existed for agricultural irrigation. Annual precipitation is about 1,400 mm and over 60% of them occur in the summer (Song et al., 2007). Drinking waters for residents are generally dependent on serviced pipes by municipality.

As part of an integrated study for assessing seawater intrusion in the coastal aquifer, a monitoring well field consisting of 15 wells (A series wells) was constructed. Depths of the wells range between 0.93 and 16 m. The monitoring wells were fully screened or left open except for upper a few meters. Surface elevations of the wells are between 0.00 and 3.03 m above mean sea level. In addition to these wells, there have been two wells (O series wells) of 60 m depth, which were originally developed as a monitoring station of SIMN managed by KARICO (Korea Agricultural & Rural Infrastructure Corporation, now KRC) and MAF (Ministry of Agriculture and Forestry). At these wells, automatic consecutive monitoring of water levels, electrical conductivities and water temperatures has been conducted.

From geologic logging data obtained during the monitoring well construction, there generally exist three hydrogeologic layers. The uppermost layer is a reclamation soil, which constitutes mostly surface of the paddy fields and it is generally classified into silty loam or silty clay loam (Fig. 2). Thickness of the reclamation soil ranges from 0.9 to 2.7 m. Below the reclamation layer, a weathered layer (sandy loam or loam) is encountered. Thickness of this layer is between 2.3 and 15 m. The upper two layers are main water bearing units in this area. The bottom layer is a fresh to slightly fractured sedimentary rock, which is intruded by volcanic rocks. Hydraulic conductivities of the three layers are in the orders of 10^{-4}, 10^{-3} and 10^{-5} cm/sec, respectively (Song et al., 2007).

Water levels in the study area were between 0.2-3 m below ground surface (measurement at 21 April of 2005). At some monitoring wells mainly covering the central and lower parts of the study site, they showed lower values than

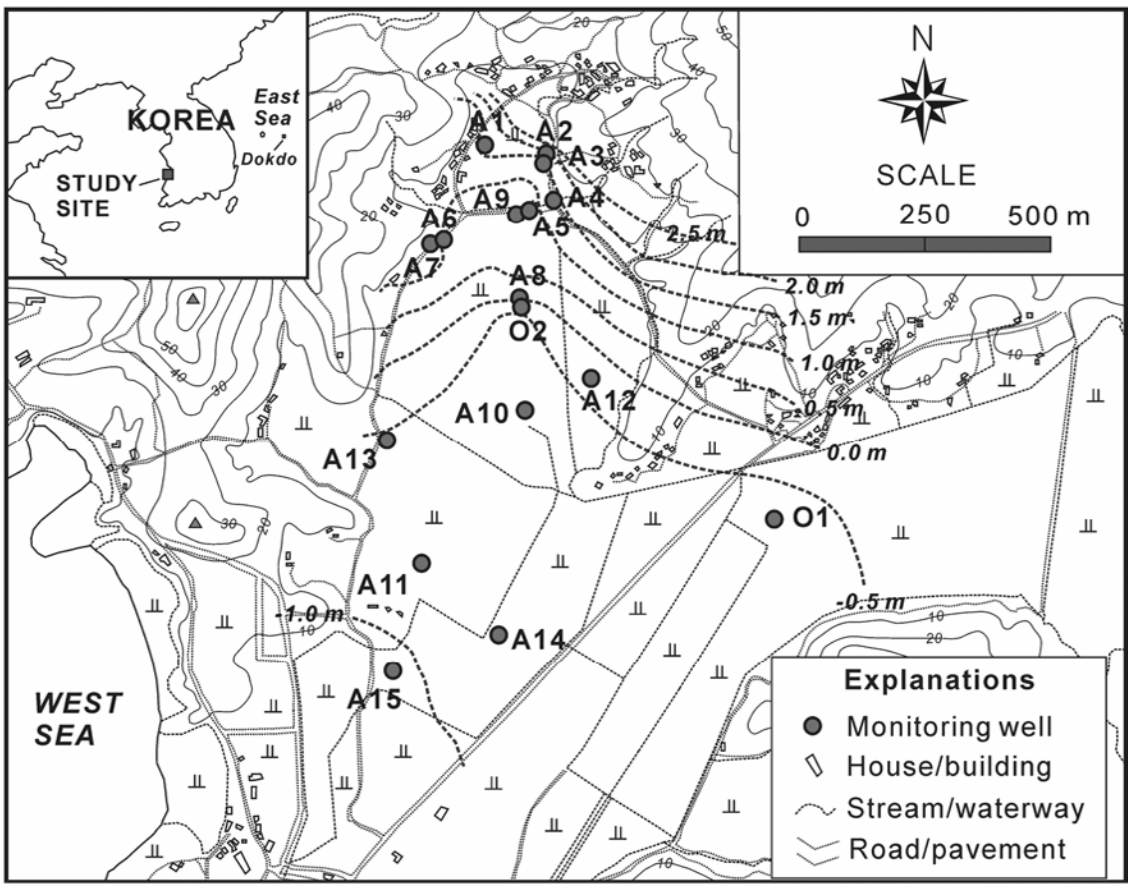

Fig. 1. Location of the studied area showing locations of the groundwater monitoring wells and water level contours (m, amsl). The figure was modified from Song et al. (2007).

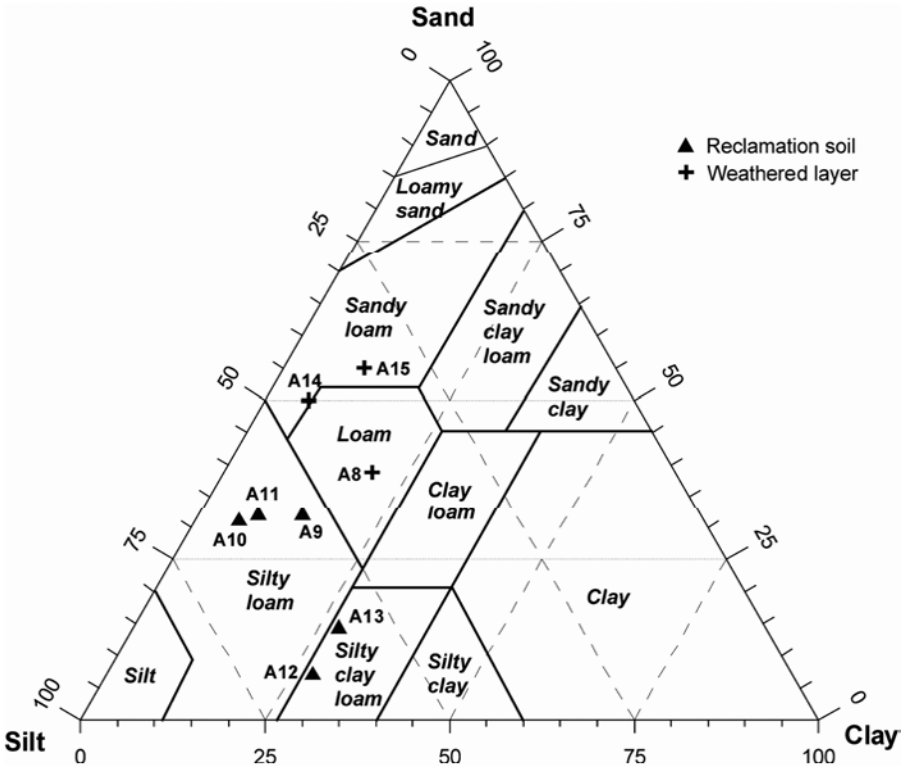

Fig. 2. Classification of particles obtained from the top reclamation soil and the weathered layer.

mean sea level (see Fig. 1). The relatively lower water levels around the wells O2 and A8 are attributed to groundwater pumping for agricultural irrigation. Groundwaters generally flow from NE to SW direction towards the coast. Water levels of the monitoring wells are mostly affected by irrigation pumping, site precipitation and tidal fluctuation. Magnitude of their annual fluctuation is restricted within 2 m but they are generally decreasing with time (Song et al., 2007).

2.2. Groundwater Chemistry Data

For this study, groundwater samples were collected from the 15 monitoring wells in January (A1-A8) and April (A9-A15) of 2005. Prior to sampling, pH, EC (electrical conductivity) and TDS (total dissolved solids) were measured in the field using standard probes. The groundwaters were analyzed for major and minor constituents including Ca, Na, K, Mg, Cl, SO_4, HCO_3 and NO_3. Anion constituents were analyzed by ion chromatography (IC, DX-120, DIONEX) and other cationic constituents were analyzed by ICP-MS (Ultramass 700, Varian), AA (5100PC, Perkin Elmer) and ICP (ICP-IIIS, Shimadzu) following USEPA standard methods. Alkalinity was determined by potentiometric titration using Gran plots.

3. RESULTS AND DISCUSSION

3.1. Basic Statistics and General Chemistry

Major constituents of groundwaters are presented in Table 1. The pHs of the groundwaters were near neutral (6.3-7.9) and they were the least varying (CV=0.05). Apparent increasing trend of pH was observed with approaching the coast. Positive values of Eh indicated oxic groundwater conditions but it also showed a decreasing trend towards the coast, which reflects progressive development of anoxic condition under the paddy fields. TDS and EC showed much varying behaviors. The TDS varied between 329 and 6,946 mg/L. Simply two groups of the monitoring wells can be extracted based on the TDS levels, that is high TDS group (>2,000 mg/L) and low TDS group (<2,000 mg/L). Generally elevated EC levels compared with those of clean shallow groundwaters indicated pollution of the groundwaters by some anthropogenic or natural factors including chemical fertilizers and seawater intrusion (Kim et al., 2003a).

Among the major ions, concentrations of Na and Cl are the most varying (CVs=1.38 and 1.42, respectively) while those of SiO_2 is the least varying (CV=0.29). The former two are the most abundant constituents in seawater and thus enrichment of these ions in groundwaters is indicative of saline water intrusion in coastal aquifers (Panteleit et al., 2001). Abundance sequences of cations in groundwaters are Na>Ca>Mg>K>SiO_2 and those of anions are Cl>HCO_3>SO_4>NO_3. Interestingly, high levels of NO_3 exceeding a Korean drinking water standard (NO_3-N 10 mg/L=NO_3 44.3 mg/L) were observed especially at the uppermost residential area, which indicated groundwater pollution by leaked domestic sewage, livestock effluent or chemical fertilizers (Kim et al., 2004). The NO_3 showed a decreasing trend close to the

Table 1. Major chemical composition of the shallow groundwaters in the studied coastal area. Units are mg/L unless otherwise noted (Part of data are from Song et al. (2007)). N.d (below detection limit) was considered as 0 for further calculation.

Sample ID	pH (SU)	Eh (mV)	TDS (mg/L)	EC (μS/cm)	Na	K	Ca	Mg	SiO_2	Cl	HCO_3	SO_4	NO_3
A1	6.7	472	337	456	46	3.74	26.98	7.93	27.59	63	70	17	72.42
A2	7.2	471	565	812	98	13.47	43.16	15.34	17.05	127	152	71	21.60
A3	6.9	471	434	619	56	5.95	34.90	18.05	26.74	72	73	38	105.92
A4	7.1	475	572	771	91	12.69	36.56	19.33	26.38	94	167	58	62.93
A5	7.2	474	521	732	67	2.43	75.07	5.58	37.30	123	118	76	13.86
A6	6.3	476	290	459	45	2.97	17.81	12.04	27.26	78	18	6	80.67
A7	7.2	471	329	480	35	4.13	36.62	18.47	11.93	53	67	36	65.46
A8	6.9	237	2,090	3,340	464	53.05	114.84	102.45	24.94	807	289	233	n.d
A9	7.0	241	581	848	79	5.34	83.89	18.79	24.94	152	109	105	n.d
A10	7.5	242	4,196	6,010	1,011	102.05	191.47	192.52	21.25	1,487	719	470	n.d
A11	7.9	236	5,658	8,310	1,737	103.71	118.75	187.83	27.15	2,207	829	445	n.d
A12	7.5	240	767	999	164	19.20	22.28	18.56	21.19	148	295	55	20.20
A13	7.2	269	6,946	11,590	2,003	117.73	138.07	298.81	14.03	3,541	207	624	n.d
A14	7.4	254	2,941	4,180	627	57.57	207.21	107.38	17.69	983	677	263	n.d
A15	7.4	255	2,289	3,320	393	43.12	247.60	75.22	16.68	710	558	244	n.d
Mean	7.2	352	1,901	2,862	461	36.48	93.01	73.22	22.81	710	290	183	29.54
S.D[a]	0.4	117	2,142	3,390	637	41.30	74.38	89.09	6.58	1,010	269	193	37.03
C.V[b]	0.05	0.33	1.13	1.18	1.38	1.13	0.80	1.22	0.29	1.42	0.93	1.05	1.25
Dis[c]	Nor	No	Log	Log	Log	Log	Log	Log	Nor	Log	Log	Log	No
Sea[d]	8.0	256	NA[e]	39,980	8,497	380.81	443.36	1,214.02	0.33	16,716	115	3,025	0.94

[a]Standard deviation

[b]Coefficient of variation

[c]Distribution determined at p=0.05 (Nor=normal, No=neither normal nor log-normal, Log=log-normal)

[d]Mean values of seawaters obtained from the off coast of Incheon (n=3)

[e]Not available

Table 2. Cross-correlations among major chemical constituents of the shallow groundwaters. Values in the lower triangle matrix indicate the correlations and those in the upper triangle are the probabilities that the two are uncorrelated. Substantially large correlation values (≥0.70) are bolded.

Para.	pH	Eh	TDS	EC	Na	K	Ca	Mg	SiO_2	Cl	HCO_3	SO_4	NO_3
pH	-	0.0292	0.0331	0.0559	0.0408	0.0246	0.0554	0.0830	0.3453	0.0956	0.0007	0.0359	0.0126
Eh	-0.56	-	0.0107	0.0154	0.0228	0.0048	0.0050	0.0142	0.3132	0.0285	0.0032	0.0058	0.0003
TDS	0.55	-0.64	-	0.0001	0.0001	0.0001	0.0131	0.0001	0.2690	0.0001	0.0070	0.0001	0.0204
EC	0.50	-0.61	**0.99**	-	0.0001	0.0001	0.0202	0.0001	0.2480	0.0001	0.0185	0.0001	0.0260
Na	0.53	-0.58	0.99	0.99	-	0.0001	0.0495	0.0001	0.3467	0.0001	0.0165	0.0001	0.0396
K	0.58	-0.69	**0.98**	**0.96**	**0.95**	-	0.0070	0.0001	0.2543	0.0001	0.0017	0.0001	0.0140
Ca	0.50	-0.68	0.62	0.59	0.51	0.66	-	0.0162	0.2283	0.0413	0.0008	0.0040	0.0036
Mg	0.46	-0.62	**0.98**	**0.99**	**0.97**	**0.98**	0.61	-	0.2020	0.0001	0.0202	0.0001	0.0306
SiO_2	-0.26	0.28	-0.31	-0.32	-0.26	-0.31	-0.33	-0.35	-	0.2471	0.5248	0.2430	0.4773
Cl	0.45	-0.56	**0.98**	**0.99**	**0.98**	**0.94**	0.53	**0.98**	-0.32	-	0.0494	0.0001	0.0408
HCO_3	**0.77**	**-0.71**	0.66	0.60	0.61	**0.74**	**0.77**	0.59	-0.18	0.52	-	0.0065	0.0114
SO_4	0.54	-0.67	**0.98**	**0.98**	**0.95**	**0.98**	**0.70**	**0.99**	-0.32	**0.96**	0.67	-	0.0081
NO_3	-0.63	**0.80**	-0.59	-0.57	-0.54	-0.62	**-0.70**	-0.56	0.20	-0.53	-0.63	-0.65	-

coastline and NO_3 was not detected at the monitoring wells in the proximity of the coast, which may be derived from anoxic condition formed in the paddy fields. But in the monitoring wells near the coast, K, Ca, Mg and SO_4 were also enriched.

Table 2 shows correlations among the field parameters and the major constituents. The pH showed a highly positive correlation (r=0.77) with HCO_3 and a moderately negative correlation (r=-0.63) with NO_3. The positive correlation (r=0.80) between Eh and NO_3 indicated more oxic conditions at the bottom of the small mountains (the uppermost residential area). TDS, EC and SO_4 showed profound cor-

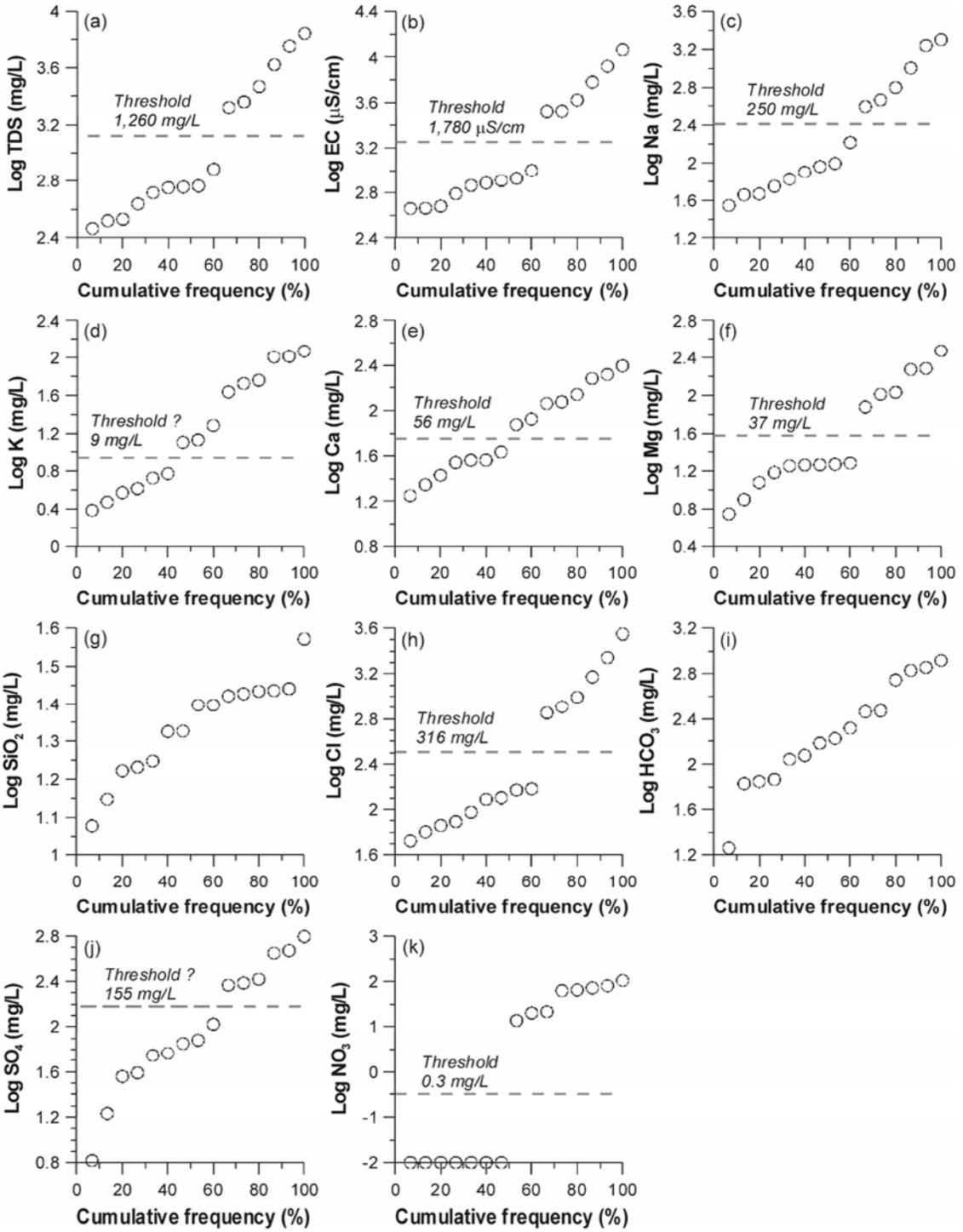

Fig. 3. Cumulative frequency plots for chemical constituents of the groundwaters also showing threshold values graphically determined.

relations with most of the other ions, which implied that much of the groundwaters were affected by saline waters enriched with most of the major ions except for SiO_2 and NO_3 (see seawater values in Table 1).

Cumulative frequency plots of chemical constituents are useful to discriminate between background or ambient and affected values by certain factors such as seawater intrusion or anthropogenic contamination (Park et al., 2005; Lee and Song, 2007). As already seen in Table 1, the chemical parameters of the groundwaters in this study generally showed abrupt increasing trends (Fig. 3). Taking the mean values between the breaks, they may be considered as the thresh-

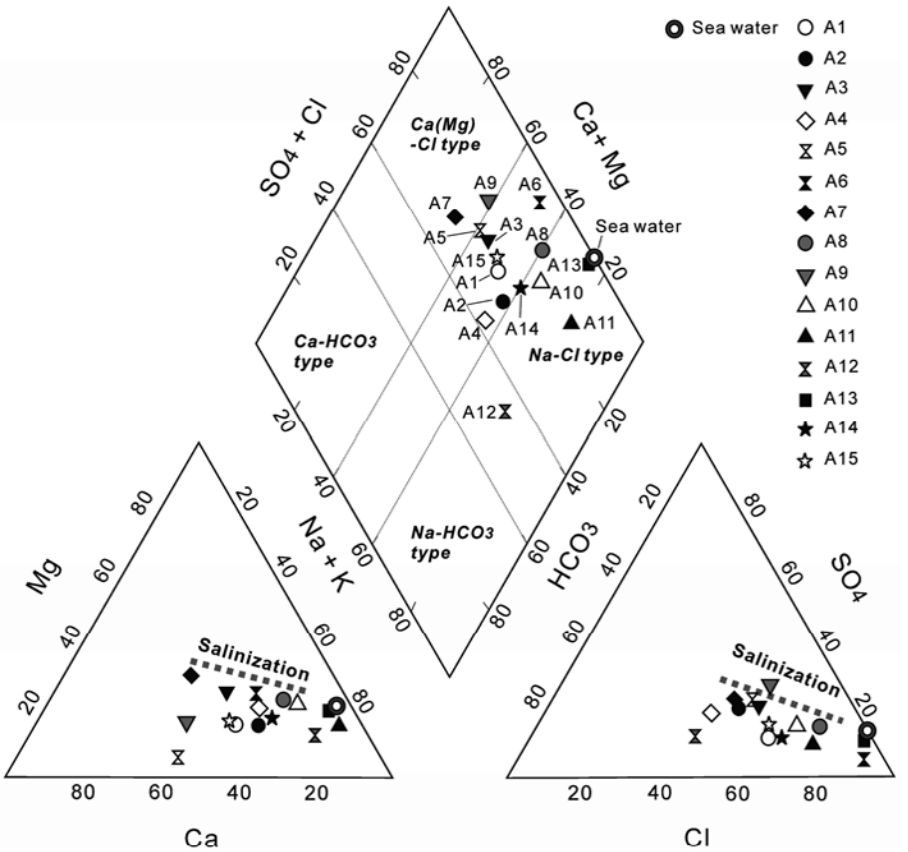

Fig. 4. Piper plot of major chemical compositions of the groundwaters.

olds differentiating the two groups. Among the analyzed 11 parameters, some of them (K, SiO_2, HCO_3, SO_4) were difficult to determine the threshold values because they were increasing consecutively without any substantial increase of values or breaks. In the mean time, considering the relatively high values of the thresholds (e.g., TDS=1,260 mg/L, Cl=316 mg/L), the higher values than them can strongly indicate effect of the seawater intrusion even though the values below the thresholds may not necessarily indicate that the groundwaters are not affected by the saline water. Furthermore, single parameter cannot determine whether the groundwater is affected or not.

A Piper plot of major chemical compositions of the groundwaters and the seawater is shown in Figure 4. From the plot, two principal groundwater facies are identified, which are Ca(+Mg)-Cl(+SO_4) and Na-Cl types. Monitoring wells (A8, A10, A11, A14, A13) showing Na-Cl type of groundwaters are the most proximal to the coast. Major chemical composition of this typed groundwater is the most similar to that of the seawater, which strongly indicated that the groundwaters were evidently affected by the very saline water (Pulido-Leboeuf, 2004). Substantial proportions of the groundwaters showed a transition or mixed type between the two distinctive facies. The monitoring wells belonging to this transition type are mostly located in the uppermost residential area. This transition typed groundwaters appeared to be affected by both saline water intrusion and anthropogenic contamination with NO_3 (see Table 1). Spatial region of the Ca-Cl type water may be a leading edge of the seawater plume (Jeen et al., 2001) but in this case it was not distinctive.

Groundwater at well A12 showed the most peculiar chemical composition compared with the groundwaters in surrounding area. The groundwater at the well was relatively enriched with HCO_3 and NO_3. The very shallow monitoring well (well depth=1.2 m) may be affected directly by rainwater infiltration (Song et al., 2007), accompanied with high levels of NO_3 derived from surface origin such as chemical fertilizers. In the mean time, spatial distribution of the groundwater facies appeared not distinctive with respect to distance from the coast but rather mixed, which may be attributed to configuration of the monitoring wells tapping the multiple hydrogeological layers and to facies determination based on a limited number of major ions. From the lower two triangles in the Piper plot, it was inferred that the groundwater salinization occurred via cation exchange reaction and mixing between two end members (fresh or less affected groundwater and the seawater).

Table 3 shows minor constituents in the groundwaters. Distribution of some minor constituents, especially F and Al, showed similar trend of that of NO_3. At upgradient wells (A1-A7), the two constituents occurred even at trace

Table 3. Minor chemical composition of the shallow groundwaters in the studied coastal area. Br concentration is not used due to low reliability of analysis. Units are mg/L.

Sample ID	F	Al	Cu	Fe	Mn	Zn	NO_2	PO_4
A1	0.266	0.021	n.d	0.005	0.308	0.050	n.d	n.d
A2	0.381	0.014	n.d	n.d	0.896	n.d	2.840	n.d
A3	0.217	0.006	n.d	n.d	0.223	0.008	1.228	n.d
A4	0.210	0.010	n.d	n.d	0.514	0.021	n.d	n.d
A5	0.223	0.008	n.d	n.d	0.026	n.d	n.d	n.d
A6	0.160	0.020	n.d	0.006	0.026	0.008	n.d	n.d
A7	0.312	0.008	n.d	n.d	0.107	0.015	n.d	n.d
A8	n.d	n.d[a]	n.d	n.d	0.125	n.d	n.d	n.d
A9	n.d	n.d	n.d	n.d	0.686	n.d	n.d	n.d
A10	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
A11	n.d	n.d	n.d	n.d	0.749	n.d	n.d	n.d
A12	n.d	0.320	n.d	0.152	n.d	n.d	n.d	n.d
A13	n.d	n.d	n.d	n.d	0.437	n.d	n.d	n.d
A14	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
A15	n.d	n.d	n.d	n.d	0.123	n.d	n.d	n.d
Mean	0.118	0.027	n.d	0.011	0.281	0.007	0.271	n.d
S.D[b]	0.139	0.081	n.d	0.039	0.304	0.014	0.778	n.d
C.V[c]	1.18	3.00	NA[d]	3.60	1.08	2.00	2.87	NA
Sea[e]	2.348	0.016	0.003	1.268	0.090	0.015	NA	0.144

[a]Not detected
[b]Standard deviation
[c]Coefficient of variation
[d]Not available
[e]Values of seawaters obtained from the off coast of Incheon (n=3)

levels while they were mostly depleted at the other downgradient wells (A8-A15). Therefore, it appeared that the two parameters might be potentially important criteria to differentiate the groundwaters affected by seawater intrusion from those not or less affected. But these criteria may not be necessarily plausible or reasonable but can be coincident because concentrations of Br and F in the seawaters are higher than the groundwaters and hence simple mixing between them would elevate the concentrations (see Table 3). Or it may be caused by seasonal variation due to different sampling time (January and April). No Cu and PO_4 were detected at all the wells. The other constituents including Fe, Mn, Zn and NO_2 were also observed at very low concentrations and thus their difference between the monitoring wells appeared not significantly meaningful. In the minor constituents, A12 well also showed much different ionic concentrations.

3.2. Ionic Ratios

Ionic ratios of groundwaters have been often used to evaluate seawater intrusion in coastal areas (Sánchez-Martos et al., 2002; Kim et al., 2003b; El Moujabber et al., 2006). Table 4 shows some selected ionic ratios of the groundwaters. Values of HCO_3/Cl, indicative of freshwater recharge, are all greater than the seawater ratio (0.0069). Generally the groundwaters of the upgradient wells have high values while those of downgradient wells have low values. The ratios gradually increase and approach the seawater value as TDS increases (Fig. 5), which indicated increase in influence of seawater intrusion. As previously noted, TDS is a perfect surrogate for Cl (r=0.98). Consequently the ratio (HCO_3/Cl) can be a good indicator for salinization due to the seawater encroachment. Ratios of Na/Ca, indicating cation exchange reaction (Edet and Okereke, 2001), showed some mixed behavior but it mostly increased with increase of TDS. The ratios of Na/Cl showed no significant correlation with TDS level (r^2=0.03) but they are very similar (not distinctive each other) to the seawater value (CV=0.24, see Table 4). This was derived from that the one was accompanied with the other when the seawater intrusion occurred. Thus this ratio may not be a good indicator revealing the salinization process.

Ratios of Ca/Cl exhibited generally a good negative correlation with TDS (r^2=0.56). They decreased as TDS increased, which was derived from Cl enrichment in groundwaters due to saline water intrusion. Ratios of Mg/Cl and SO_4/Cl were moderately varying (CVs=0.52 and 0.40, respectively) and they showed a moderate negative correlation with TDS. They decrease as TDS increase and thus low values of them

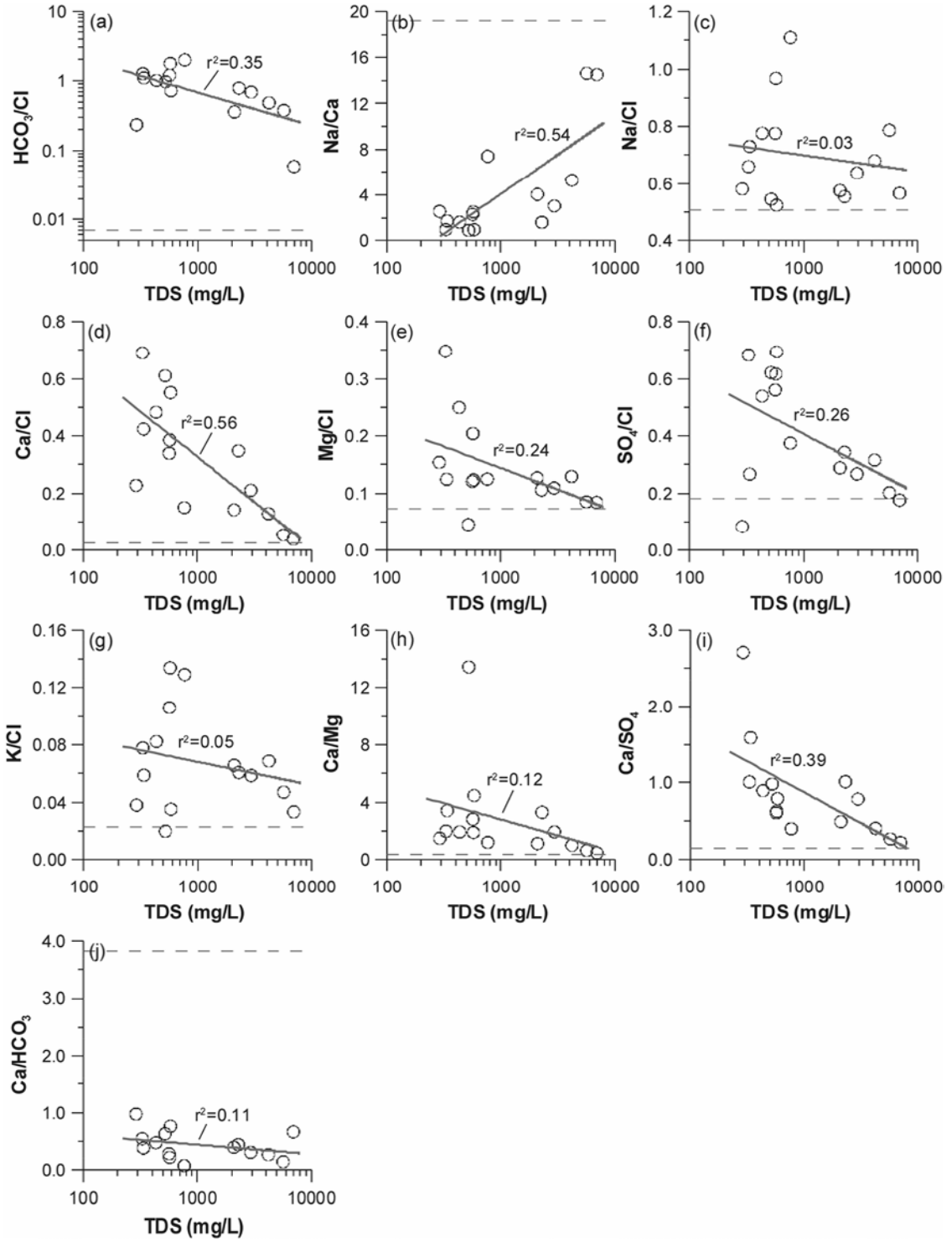

Fig. 5. Ionic ratios of groundwaters with TDS levels. Dotted line indicates the seawater ratio.

may indicate influence of seawater intrusion in coastal aquifers. Ratio of K/Cl showed a very weak correlation with TDS. For a given range of TDS, it is greatly varying. Therefore it may not be a good criterion for evaluating seawater intrusion. Ratios of Ca/Mg and Ca/HCO_3 are not closely correlated with TDS and they are not generally varying in spite of increase of TDS. The Ca/SO_4 showed a moderate negative correlation with TDS. Thus low Ca/SO_4 indicated high TDS and hence effect of seawater intrusion.

In the mean while, some ionic ratios appeared useful to delineate degree of salinization effect for the groundwaters, but it should be noted that they may be disturbed by certain

Table 4. Ionic ratios of the shallow groundwaters in the studied coastal area. Units are mg/L/mg/L.

Sample ID	HCO_3/Cl	Na/Ca	Na/Cl	Ca/Cl	Mg/Cl	K/Cl	SO_4/Cl	Ca/Mg	Ca/SO_4	Ca/HCO_3
A1	1.1018	1.7228	0.7300	0.4237	0.1245	0.0587	0.2670	3.4023	1.5871	0.3846
A2	1.2004	2.2857	0.7765	0.3397	0.1207	0.1060	0.5602	2.8136	0.6064	0.2830
A3	1.0122	1.6095	0.7767	0.4826	0.2496	0.0823	0.5383	1.9335	0.8965	0.4768
A4	1.7716	2.5057	0.9675	0.3861	0.2041	0.1340	0.6160	1.8914	0.6268	0.2179
A5	0.9668	0.8929	0.5448	0.6101	0.0454	0.0198	0.6207	13.4534	0.9830	0.6311
A6	0.2337	2.5514	0.5803	0.2275	0.1538	0.0379	0.0839	1.4792	2.7108	0.9732
A7	1.2644	0.9563	0.6599	0.6900	0.3480	0.0778	0.6825	1.9827	1.0110	0.5458
A8	0.3588	4.0435	0.5751	0.1422	0.1269	0.0657	0.2888	1.1209	0.4925	0.3963
A9	0.7209	0.9511	0.5239	0.5508	0.1234	0.0351	0.6940	4.4646	0.7937	0.7640
A10	0.4840	5.2841	0.6803	0.1287	0.1295	0.0686	0.3163	0.9945	0.4070	0.2660
A11	0.3759	14.6317	0.7873	0.0538	0.0851	0.0470	0.2019	0.6322	0.2664	0.1431
A12	1.9923	7.3950	1.1095	0.1500	0.12503	0.1293	0.3751	1.2004	0.4000	0.0753
A13	0.0586	14.5118	0.5658	0.0390	0.0844	0.0332	0.1763	0.4621	0.2212	0.6657
A14	0.6883	3.02645	0.6374	0.2106	0.1091	0.0585	0.2673	1.9297	0.7879	0.3060
A15	0.7855	1.5898	0.5540	0.3484	0.1059	0.0607	0.3437	3.2917	1.0139	0.4436
Mean	0.8677	4.2639	0.6979	0.3189	0.1424	0.0676	0.4021	2.7368	0.8536	0.4382
S.D[a]	0.5478	4.5419	0.1668	0.2043	0.0747	0.0339	0.1989	3.1663	0.6243	0.2446
C.V[b]	0.63	1.07	0.24	0.64	0.52	0.50	0.49	1.16	0.73	0.56
Dis[c]	Nor	Log	Log	Nor	Log	Nor	Nor	Log	Log	Nor
Sea[d]	0.0069	19.1662	0.5083	0.0265	0.0726	0.0228	0.1810	0.3652	0.1465	3.8290

[a]Standard deviation
[b]Coefficient of variation
[c]Distribution determined at p=0.05 (Nor=normal, No=neither normal nor log-normal, Log=log-normal)
[d]Values of seawaters obtained from the off coast of Incheon (n=3)

artifacts in the course of the groundwater samplings or chemical analysis.

3.3. Cluster Analysis

It is generally known that a large amount of groundwater chemistry data can be understand by simplifying the complex and diverse relationships that exist among a set of observed parameters using some multivariate analyses (Suk and Lee, 1999). Cluster analysis groups the whole groundwater samples into a finite number of clusters and each cluster represents a specific and similar hydrochemical state of groundwater (Lee et al., 2001). In this study, the 15 groundwater sampling points (wells) were analyzed by the clustering using the chemistry data and the ionic ratios.

Before conducting the multivariate analysis, data distribution was examined for each parameter using normal probability (normal QQ) plots (Hammer et al., 2001). Only two parameters (pH and SiO_2) were normally distributed at p=0.05 without any data transformation (see Table 1). To obtain the normal distribution, the logarithmic transformation was applied for the other 11 parameters, which has been commonly applied to hydrochemistry data (Ochsenkühn et al., 1997; Reimann and Filzmoser, 2000; Lee et al., 2001). After the logarithmic transformation, normal distribution (actually normal or lognormal) was attained for all the parameters at p=0.05 except for Eh and NO_3. In spite of this log transformation, distribution of the two parameters was not improved. Thus Eh was excluded in the further statistical analysis in consideration of its low coefficient of variation (CV=0.33) and consequently low importance in these chemistry data. However, treatment of NO_3 is somewhat delicate and complicated. It appeared that NO_3 in this study might be a key constituent to represent anthropogenic effect and thus it was further considered in the data analysis even though low degree of normality was exhibited (normal at p=0.1). In addition, EC was excluded for further analysis because TDS is a perfect surrogate for EC (r=0.99).

Now the normally distributed data were standardized and scaled to equalize the influence of parameters with small and large variations using the z transformation (Auf der Heyde, 1990; Lee et al., 2001). Using the calculated z scores, the cluster analysis was conducted. All the above manipulation processes for the chemistry data were also applied for the ionic ratios (see Table 4). Among the 10 ionic ratios, only 6 ratios were selected for the cluster analysis because the other 4 ratios did not showed good potentials for the indicator of the seawater intrusion (see Fig. 5).

Resulting dendrograms are presented in Figure 6. The two dendrograms based on major groundwater chemistry and the ionic ratios showed very similar classification of the groundwater monitoring wells. According to mean ionic

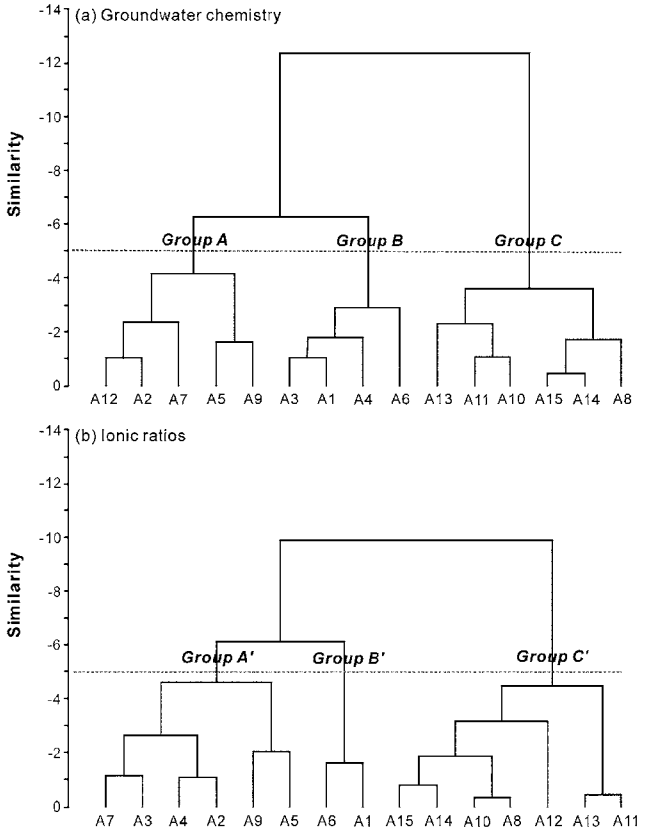

Fig. 6. Dendrograms formed using (a) major groundwater chemistry and (b) ionic ratios.

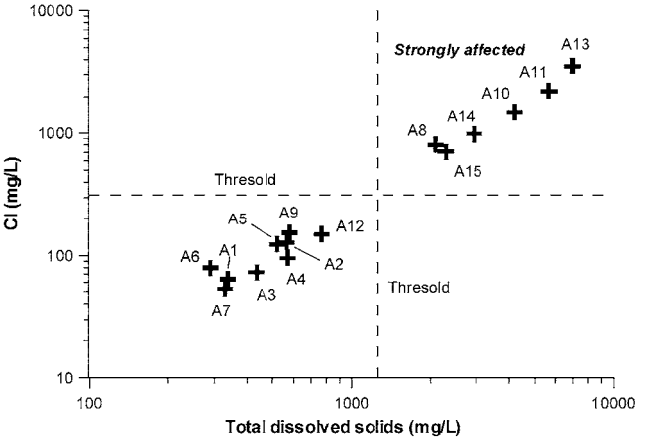

Fig. 7. Simple division of groundwater wells using TDS and Cl concentrations.

concentrations of each class (Table 5), it was inferred that the groups C and C' represented the groundwaters strongly affected by the seawater intrusion while the groups B and B' were least affected by it and they were largely affected by anthropogenic nitrate contamination due to septic effluents or chemical fertilizers. The former groups are mostly located in the proximity of the coast. The groups A and A' showed some mixed chemical compositions of both of them and they are only distributed at immediately bottom of the small mountains. Consequently it is demonstrated that some ionic ratios can be used as indicators for evaluating seawater intrusion in coastal aquifers. Actually in this case, bivariate plot of Cl and TDS (Fig. 7), which considered as the most common useful indicators for the salinization from seawater intrusion, can differentiate the groundwaters strongly affected from those less or not affected. But more delicate or sophisticated divisions would not be probable.

4. SUMMARY AND CONCLUSION

In this study, the seawater intrusion or salinization in a coastal aquifer was evaluated using groundwater chemistry

Table 5. Mean major chemical compositions of the groundwaters grouped by the cluster analysis. Units are mg/L unless otherwise noted.

Parameters	Group A	Group B	Group C	Group A'	Group B'	Group C'
Member wells	A12, A2, A7, A5, A9	A3, A1, A4, A6	A13, A11, A10, A15, A14, A8	A7, A3, A4, A2, A9, A5	A6, A1	A15, A14, A10, A8, A12, A13, A11
pH (SU)	7.2±0.2	6.8±0.3	7.4±0.3	7.1±0.1	6.5±0.3	7.4±0.3
Eh (mV)	379±127	474±2	249±13	434±94	474±3	248±12
TDS	553±157	408±125	4,020±1,958	500±100	314±33	3,555±2,169
EC (μS/cm)	774±191	576±151	6,125±3,288	710±138	458±2	5,393±3,573
Na	89±48	59±21	1,039±683	71±23	45±0	914±706
K	8.91±7.15	6.34±4.42	79.54±31.81	7.34±4.62	3.36±0.54	70.92±36.93
Ca	52.20±26.21	29.06±8.59	169.66±53.95	51.70±21.88	22.40±6.48	148.60±74.36
Mg	15.35±5.64	14.34±5.32	160.70±82.90	15.93±5.26	9.99±2.91	140.40±92.81
SiO_2	22.48±9.59	26.99±0.54	20.29±5.07	24.06±8.77	27.43±0.23	20.42±4.64
Cl	120±39	77±13	1,622±1,090	103±37	70±10	1,412±1,140
HCO_3	148±87	82±62	546±248	114±40	44±36	511±245
SO_4	69±25	30±23	380±158	64±25	11±7	333±189
NO_3	24.22±24.59	80.49±18.44	0.00±0.00	44.96±39.98	76.55±5.83	2.89±7.64

data and ionic ratios. Major ionic compositions effectively indicated effects of the seawater intrusion and especially Cl and TDS concentrations are the simplest indicators for the salinization process. In this study, values of Cl and TDS, greater than 316 and 1,260 mg/L, respectively, strongly indicated effect of the saline water intrusion. Besides of the major chemical compositions, ionic ratios of them can be efficiently used to delineate seawater intrusion. Among them, the ratios, HCO_3/Cl, Na/Ca, Ca/Cl, Mg/Cl and Ca/SO_4 appeared the most useful. Cluster analysis based on these ratios produced an equivalent result to that using the major chemical compositions.

In coastal area, even under the non-pumping normal condition, a saline water would intrude the fresh groundwater and forms their interface or a transition zone in the subsurface. Thus within a certain lateral extent from the coast, groundwater salinity would increase as the well depth increases. To determine whether the groundwater salinity is derived from anthropogenic origin such as excessive groundwater use or it is a natural phenomenon, consecutive groundwater monitoring of water level, EC and groundwater chemistry is required for many years.

ACKNOWLEDGEMENTS: The research was supported by a grant (code number 3-3-2) from Sustainable Water Resources Research Center of 21st Century Frontier Research Program. Two anonymous reviewers and Editor Prof. Kang-Kun Lee at Seoul National University greatly improved the initial manuscript.

REFERENCES

Auf der Heyde, T.P.E., 1990, Analyzing chemical data in more than two dimensions. Journal of Chemical Education, 67, 461–469.

Benkabbour, B., Toto, E.A. and Fakir, Y., 2004, Using DC resistivity method to characterize the geometry and the salinity of the Plio-quaternary consolidated coastal aquifer of the Mamora plain, Morocco. Environmental Geology, 45, 518–526.

Edet, A.E. and Okereke, C.S., 2001, A regional study of saltwater intrusion in southeastern Nigeria based on the analysis of geoelectrical and hydrochemical data. Environmental Geology, 40, 1278–1279.

El Moujabber, M., Bou Samra, B., Darwish, T. and Atallah, T., 2006, Comparison of different indicators for groundwater contamination by seawater intrusion on the Lebanese Coast. Water Resources Management, 20, 161–180.

Hammer, Ø., Harper, D.A.T. and Ryan, P.D., 2001, PAST: paleontological statistics software package for education and data analysis. Palaeontologia Electronica, 4(1), 9.

Hwang, S., Shin, J., Park, I. and Lee, S., 2004, Assessment of seawater intrusion using geophysical well logging and electrical soundings in a coastal aquifer, Youngkwang-gun, Korea. Exploration Geophysics, 35, 99–104.

Jeen, S.W., Kim, J.M., Ko, K.S., Yum, B.W. and Chang, H.W., 2001, Hydrogeochemical characteristics of groundwater in a mid-western coastal aquifer system, Korea. Geosciences Journal, 5(4), 339–348.

Kim, J.H., Kim, R.H. and Chang, H.W., 2003a, Hydrogeochemical characterization of major factors affecting the quality of shallow groundwater in the coastal area at Kimje in South Korea. Environmental Geology, 44, 478–489.

Kim, J.H., Yum, B.W., Kim, R.H., Koh, D.C., Cheong, T.J., Lee, J.H. and Chang, H.W., 2003b, Application of cluster analysis for the hydrogeochemical factors of saline groundwater in Kimje, Korea. Geosciences Journal, 7(4), 313–322.

Kim, K., Rajmohan, N., Kim, H.J., Hwang, G.S. and Cho M.J., 2004, Assessment of groundwater chemistry in a coastal region (Kunsan, Korea) having complex contaminant sources: a stoichiometric approach. Environmental Geology, 46, 763–774.

Lee, J.Y., Cheon, J.Y., Lee, K.K., Lee, S.Y. and Lee, M.H., 2001, Statistical evaluation of geochemical parameter distribution in a ground water system contaminated with petroleum hydrocarbons. Journal of Environmental Quality, 30, 1548–1563.

Lee, J.Y. and Song, S.H., 2007, Evaluation of groundwater quality in coastal areas: implications for sustainable agriculture. Environmental Geology, 52, 1231–1242.

MAF (Ministry of Agriculture and Forestry of Korea) and KARICO (Korea Agricultural & Rural Infrastructure Corporation), 2003, An Annual Report on Investigation of Seawater Intrusion. MAF and KARICO, Uiwang, Korea, 209 p. (in Korean)

Murad, A.A. and Krishnamurthy, R.V., 2004, Factors controlling groundwater quality in Eastern United Arab Emirates: a chemical and isotopic approach. Journal of Hydrology, 286, 227–235.

Ochsenkühn, K.M., Kontoyannakos, J. and Ochsenkühn-Petropulu, M., 1997, A new approach to a hydrochemical study of groundwater flow. Journal of Hydrology, 194, 64–75.

Panteleit, B., Kessels, W., Kantor, W. and Schulz, H.D., 2001, Geochemical characteristics of salinization-zones in the Coastal Aquifer Test Field (CAT-Field) in North-Germany. In: Proceeding of 5th International Conference on Saltwater Intrusion and Coastal Aquifers-Monitoring, Modeling, and Management, Essaouira, Morocco, 1–11.

Park, S.C., Yun, S.T., Chae, G.T. and Lee, S.K., 2002, Hydrogeochemistry of shallow groundwaters in western coastal area of Korea: a study on seawater mixing in coastal aquifers. Journal of KoSSGE, 7(1), 63–77.

Park, S.C., Yun, S.T., Chae, G.T., Yoo I.S., Shin, K.S., Heo, C.H. and Lee, S.K., 2005, Regional hydrochemical study on salinization of coastal aquifers, western coastal area of South Korea. Journal of Hydrology, 313, 182–194.

Pulido-Leboeuf, P., 2004, Seawater intrusion and associated processes in a small coastal complex aquifer (Castell de Ferro, Spain). Applied Geochemistry, 19, 1517–1527.

Reimann, C. and Filzmoser, P., 2000, Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. Environmental Geology, 39, 1001–1014.

Sánchez-Martos, F., Pulido-Bosch, A., Molina-Sánchez, L. and Vallejos-Izquierdo, A., 2002, Identification of the origin of salinization in groundwater using minor ions (Lower Andarax, Southeast Spain). Science of the Total Environment, 297, 43–58.

Sherif, M., El Mahmoudi, A., Garamoon, H., Kacimov, A., Akram, S., Ebraheem, A. and Shetty, A., 2006, Geoelectrical and hydrogeochemical studies for delineating seawater intrusion in the outlet of Wadi Ham, UAE. Environmental Geology, 49, 536–551.

Song, S.H., 2006, Spatial analysis of small-loop electromagnetic survey data in a seawater intrusion region. Exploration Geophysics, 37, 114–120.

Song, S.H., Lee, J.Y. and Park, N., 2007, Use of vertical electrical

soundings to delineate seawater intrusion in a coastal area of Byunsan, Korea. Environmental Geology, 52, 1207–1219.

Suk, H. and Lee, K.K., 1999, Characterization of a ground water hydrochemical system through multivariate analysis: clustering into ground water zones. Ground Water, 37, 358–366.

Vengosh, A., Gill, J., Lee Davisson, M. and Bryant Hudson, G., 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 Resources Research, 38(1), 91-9-17.

Manuscript received September 4, 2006
Manuscript accepted August 29, 2007