Application of cluster analysis for the hydrogeochemical factors of saline groundwater in Kimje, Korea

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ABSTRACT: The main hydrogeochemical characteristics of shallow groundwater in the coastal area at Kimje city, Korea, have been identified in the present study. From cluster analysis, the groundwater in the study area is classified into four groups (A, B, C, and D). Groundwaters in B, C, and D groups are strongly affected by the present seawater and the trapped old seawater because the area including B, C, and D groups contacts the Yellow Sea and contains the reclaimed land. They also are governed by reduction processes. On the other hand, groundwater in group A has been largely affected by chemical fertilizers because its land has been used for the agricultural activities for a long time. As groundwater flows from group A to group D according to its path, the governing factor of the groundwater quality gradually tends to change from chemical fertilizers into reduction processes and seawater intrusion.

Key words: cluster analysis, seawater intrusion, chemical fertilizer, reduction processes, Kimje

1. INTRODUCTION

Groundwater in the coastal area is relatively vulnerable to the salinization by the natural seawater, which makes groundwater unsuitable for the drinking or agricultural water. Also, heavy pumping and excessive use of groundwater near the costal area can increase the groundwater salinization. This salinization is the most widespread phenomenon of groundwater contamination (Barker et al., 1998; Bear et al., 1999; Cruz and Silva, 2000; Giménez and Morell, 1997). In Korea, most researches on the groundwater salinization have been focused on Jeju Island where groundwater is a unique source of drinking water (Choi and Kim, 1989; Park and Oh, 1996). However, the results of such researches on Jeju Island do not apply to the other coastal areas of the Korean peninsula due to the islands unique hydrogeological settings. The Jeju Island is geologically characterized by volcanic sediments, whereas the other

coastal areas by igneous or sedimentary rocks. Therefore, researches on the groundwater salinization in the other coastal areas of Korean peninsula are required for the exploitation and management of the water resources.

The study area has been used for agriculture for a long time, and thus both the irrigation system and groundwater are used as agricultural water sources. Since the groundwater has been severely contaminated by salinization, most agricultural water depends on the irrigation system. This implies that the groundwater salinization may have been caused by natural processes rather than agricultural activities or heavy pumping. Other important factors, however, should be also considered. A part of the study area is the reclaimed area of the developed tideland containing a large amount of organic matter and trapped old seawater. Since the tideland has been reclaimed to increase land space, subsurface and groundwater environments have been changed. In this study, seawater trapped by the reclamation of the tideland is referred to 'trapped old seawater', while seawater causing the tidal level change is referred to 'present seawater'.

The purpose of the study is to identify and evaluate the main factors affecting the groundwater quality. To accomplish this purpose, physico-chemical properties of groundwater have been examined. Also, based on the analyzed data, statistical method has been used to classify and characterize the groundwater quality.

2. GEOLOGY AND HYDROGEOLOGY

The study area is located in Kimje, the southwestern part of the Korean peninsula, which is bounded by the Yellow Sea and surrounded by the Mankyoung River and the Shinpyoung Stream that is a tributary of the Dongjin River (Fig. 1). Every year large amounts of sediment with organic matter have been transported from the land to the Yellow Sea by the rivers, and
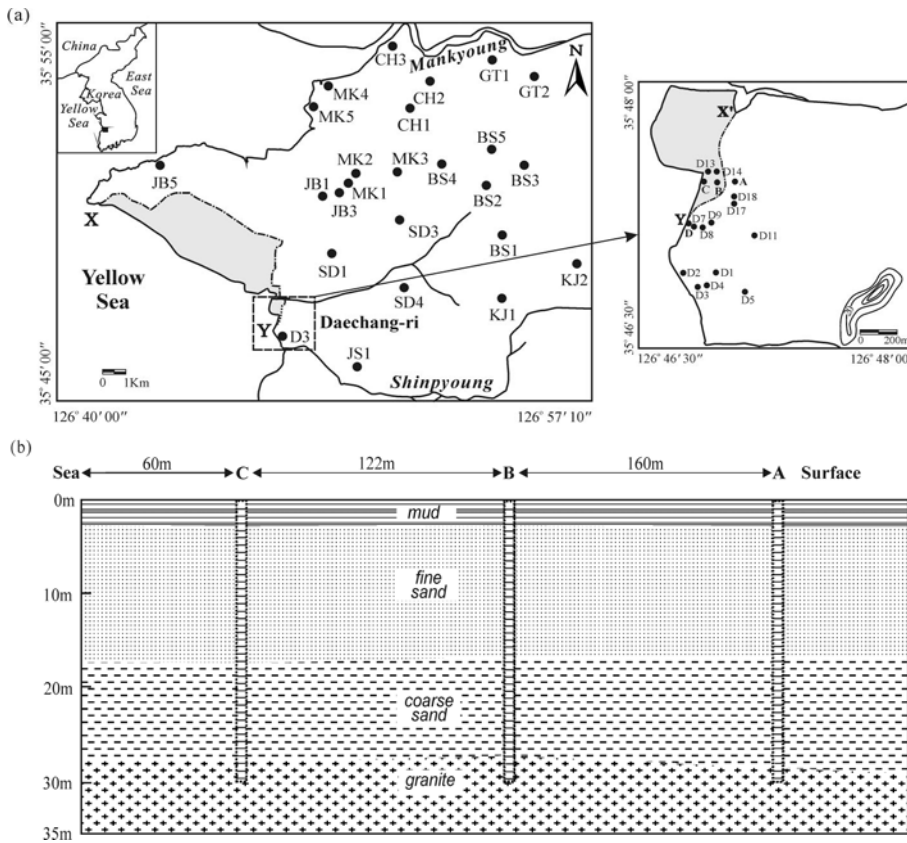
Fig. 1. (a) Location map of the study area and sampling sites (XY and X′Y: the coastline of 1910). (b) Lithostratigraphy of monitoring wells, A, B, and C.

steadily accumulated at the contact area between the Yellow Sea and these rivers. As a result, a wide tideland has been developed in the study area. The tideland has been reclaimed for the agricultural activities due to the increasing population, and it is assumed that the reclamation has been carried out from the inland area to the coastal area. As a consequence of the reclamation, the shape of coastline of the study area has been changed. In 1910, it was on the right side of the dashed XY and X′Y lines, then it moved to the left side of the lines in 1996 (Fig. 1a).

Core samples from the three monitoring wells (A, B, and C), which were installed in the sequence of C, B, and A from the coastline, can provide the geological information. The bedrock is Jurassic granite, which belongs to the intermediate and acidic rock (Park et al., 2001). And Quaternary alluvium mainly composed of coarse sand, fine sand and mud layers overlays the granite (Fig. 1b). The depth of the layers below the surface is 0–4 m for the mud layer, 4–17 m for the fine sand layer, and 17–28 m for the coarse sand layer. Additionally, gravel which is remnant of weathered granite lies between the granite and the coarse sand layer. According to slug tests, the hydraulic conductivity of the coarse sand layer ranges from $1.1×10^{-1}$ to $2.6×10^{-3}$ cm/sec and that of the fine sand layer is $1.5×10^{-6}$ cm/sec (Kim, 2001). These results represent that the study area has a confined aquifer and that the main groundwater flow occurs through lower coarse sand layer rather than upper fine sand layer.

The groundwater level ranges from 16 m a.m.s.l. inlnad area (e.g. BS2, BS3, and BS5 wells) to near 0 m a.m.s.l. at the coastal area (e.g. A, B, C, and D wells) with a gradually lowering trend close to the coastline. Therefore, groundwater flows from the inland to the coastal area throughout the coarse sand layer, and its flow rate tends to become slow close to the coastline.

3. METHODS

3.1. Sampling and Chemical Analysis

Total of 53 groundwater samples were colleted from 37 wells and 4 monitoring wells (A, B, C, and D) after purging at least two times of well volume. Sampling, preservation and chemical analysis were conducted following the standard procedures devised by Eaton et al. (1995). The first survey was conducted in March 1999, and the second in July 1999. Temperature (T), redox potential (Eh), electrical conductivity (EC) and pH were measured using temperature-compensated electronic meters in the field. Alkalinity was determined by the Gran titration method using 0.1NHCl. Dissolved oxygen (DO) was measured by the Winkler iodometric titration method. For the analysis of cations and anions, groundwaters were filtered in the field with a hand-held syringe using 0.45 μm membrane filters. Concentrated HNO_3 was added in the samples to lower the pH of samples less than 2 to prevent the absorption to the container surface and precipitation of cations. Cations (Na^+, Mg^{2+},

K^+, Ca^{2+}, Fe^{2+}, Mn^{2+}, and Sr^{2+}) were analyzed by inductively coupled plasma-atomic emission spectrometer (Jobin Yvon 138 Ultrace ICP-AES) at Korea Basic Science Institute (KBSI). Anions (Cl^-, SO_4^{2-}, NO_3^-, and Br^-) were analyzed by ion chromatography (Dionex DX-500 IC) with an AS-40 auto sampler at Seoul National University (SNU), and iodide of low level was analyzed using the UV-visible spectrometer at SNU following Eaton et al. (1995). Total organic carbon (TOC) was analyzed using total organic carbon analyzer at the Institute of Environmental Science and Engineering in SNU. δD, $\delta^{18}O$, and $\delta^{13}C$ were analyzed by VG Prism stable isotope ratio mass spectrometer at the KBSI. The analytical reproducibility was $\pm 0.1‰$ for $\delta^{18}O$, $\pm 1‰$ for δD, and $\pm 0.1‰$ for $\delta^{13}C$. All oxygen, hydrogen and carbon isotopes were reported in the usual δ notation relative to the V-SMOW for oxygen and hydrogen and the V-PDB for carbon.

In addition to the groundwater sampling, continuous and regular EC and groundwater level was monitored every 15 minutes from July 23 to August 22, 2000, using Orpheus installed at the depth of 23 m in monitoring well C, to inspect the tidal effect on the groundwater quality.

3.2. Statistical Analysis

Seventeen physico-chemical compositions, including cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, and Sr^{2+}), anions (Cl^-, Br^-, NO_3^-, HCO_3^-, and SO_4^{2-}), T, DO, pH, EC, and TOC were used for the cluster analysis. Cluster analysis (CA) was performed using the Wards method. This method uses an analysis of variance approach to evaluate the distance between clusters, attempting to minimize the sum of squares of any two hypothetical clusters that can be formed at each step (Vega et al., 1998; Helena et al., 2000).

4. RESULTS

4.1. Groundwater Quality

The physico-chemical and isotopic compositions of groundwater in the study area are represented in Table 1. DO and Eh range from 0.0 mg/l to 11.1 mg/l and from 0.63 V to 0.05 V, respectively. Their values have a decreasing trend close to the coastline. In addition, Fe^{2+} and Mn^{2+} concentrations gradually increase while NO_3^- concentration decrease, as the groundwater flows from the inland area to the coast. This indicates that the condition of groundwater changes from an oxic to a suboxic/anoxic through its flow path. On the contrary, the EC value of groundwater ranges from 0.09 mS/cm to 10.70 mS/cm, and it has a rapidly increasing trend close to the coastline. Most chemical and isotopic values also show a similar trends to that of EC. These results imply that the high saline water has strongly influenced the groundwater quality close to the coastal area.

According to Kim et al. (2003), using the Piper diagram, the chemical compositions of groundwater are divided into two types, the Na-Cl and the Ca+Mg-NO_3+Cl. The former is localized in the coastal area, whereas the latter is localized in the inland area.

4.2. Cluster Analysis

Based on the standardized physico-chemical data, cluster analysis was performed to split the water sampling points into a finite number of groups (zones) with similar hydrogeochemical composition. Figure 2 shows the resulting dendrogram of the groundwater in the study area. Groundwater is classified into four groups (A, B, C, and D), which is a different grouping from the Piper diagram (Kim et al., 2003). This different grouping is mainly owing to the limited use of geochemical data in the Piper diagram. The groups by cluster analysis are discriminated by their location from the coastline. Group A is inland area and the others locate in the coastal area. Additionally, group D is on the left side of the dashed XY and X'Y lines in Figure 1a, whereas group C is on the right side of dashed XY and X′Y lines. The lines in Figure 1a are the boundary of the reclaimed area between 1910 and 1996.

To examine the chemical variation according to the groups, box plots (also called box-and-whisker plots) of individual variables are plotted. Figure 3 shows box plots for some meaningful variables related to the groundwater quality, such as DO, pH, EC, Na^+, Cl^-, NO_3^-, Fe^{2+}, HCO_3^-, and TOC. The line across the box represents the median, whereas the bottom and top of the box show the locations of the first and third quartiles (Q_1 and Q_3). The whiskers are the lines that extend from the bottom and top of the box to the lowest and highest observations inside the region defined by $Q_1-1.5 (Q_3-Q_1)$ and $Q_3+1.5 (Q_3-Q_1)$. Individual points with values outside these limits (outliers) are plotted with asterisks. By inspecting these plots it is possible to perceive difference among groups. EC, Cl^-, Na^+, Fe^{2+}, and TOC have an increasing trend in the order of groups A, B, C, and D, whereas DO and NO_3^- have the reverse trend. Also, pH is the lowest in group A. While an EC greater than 1 mS/cm is considered to be indicative of saline water intrusion (Fetter, 1994), groundwaters in groups B, C, and D are regarded as saline water, whereas the groundwaters in groups A are considered to be fresh water.

5. DISCUSSION

5.1. Group A: Chemical Fertilizer

About 35% of groundwaters in group A have higher nitrate concentration than the Korean drinking water limit (DWL: 44.3 mg/l), indicating that this group has been severely contaminated by nitrate. Considering most land of the study area have been used for the agricultural activities and groundwater is slightly acidic (5.5<pH<6.99), nitrate is thought to be of an origin from anthropogenic source, chemical fertilizers. Also,

Table 1. Physico-chemical properties of groundwater in the study area (1999).

Well	Month	pH	T (°C)	EC (mS/cm)	Eh (V)	DO (mg/l)	Cl⁻ (mg/l)	Br⁻ (mg/l)	NO₃⁻ (mg/l)	SO₄²⁻ (mg/l)	HCO₃⁻ (mg/l)	Na⁺ (mg/l)	Mg²⁺ (mg/l)	K⁺ (mg/l)	Ca²⁺ (mg/l)	Fe²⁺ (mg/l)	Mn²⁺ (mg/l)	I⁻ (µg/l)	TOC (mg/l)	δ¹³C (‰)	δD (‰)	δ¹⁸O (‰)
BS1	March	6.73	14.0	0.19	0.38	8.9	9.3	n.d.	5.3	n.d.	18.7	8.1	1.1	0.6	6.8	n.d.	n.d.	–	1.8	–	–49.2	–6.7
BS2	March	6.02	13.9	0.36	0.46	8.8	36.6	n.d.	97.4	n.d.	11.7	19.4	6.0	2.0	26.4	n.d.	n.d.	–	2.3	–	–55.0	–7.6
BS3	March	6.67	12.1	0.20	0.57	9.7	21.2	n.d.	10.2	22.0	21.1	9.4	3.3	8.0	12.5	0.1	n.d.	–	8.0	–	–	–
BS4	March	6.82	13.7	0.26	0.59	4.7	17.9	n.d.	43.6	n.d.	32.8	12.4	2.3	1.3	12.9	n.d.	n.d.	–	1.2	–	–55.1	–7.6
BS5	March	6.09	13.0	0.24	0.61	7.2	24.6	n.d.	46.3	n.d.	19.2	13.4	2.9	1.3	15.6	n.d.	n.d.	–	2.4	–	–55.0	–7.7
CH1	March	6.68	15.1	0.21	0.41	8.0	23.5	n.d.	30.5	n.d.	24.8	11.9	3.2	0.9	16.8	n.d.	n.d.	–	2.3	–	–52.9	–7.1
CH2	March	6.18	14.8	0.33	0.59	6.0	45.9	n.d.	40.7	3.6	30.9	16.4	5.6	1.5	31.1	n.d.	n.d.	–	3.0	–	–52.9	–7.3
CH3	March	6.64	14.8	0.29	0.30	7.1	34.3	n.d.	10.1	7.6	51.4	14.5	7.9	2.0	23.7	0.3	n.d.	–	3.0	–	–	–
GT1	March	6.17	14.4	0.87	0.34	3.9	151.5	n.d.	103.3	33.1	71.0	49.4	22.9	7.8	63.2	n.d.	n.d.	–	4.7	–	–51.6	–7.3
GT2	March	6.31	15.1	0.24	0.37	8.8	31.8	n.d.	26.7	1.5	27.8	14.3	2.8	0.6	18.3	n.d.	n.d.	–	2.0	–	–53.2	–7.4
JB1	March	8.55	13.4	0.35	0.35	2.2	40.6	n.d.	5.0	3.3	79.6	35.8	0.4	0.9	2.1	n.d.	n.d.	–	4.8	–	–	–
JB3	March	7.16	13.7	0.32	–	5.3	36.9	n.d.	54.8	2.5	52.8	16.1	7.1	3.4	21.0	n.d.	n.d.	–	3.0	–	–	–
JB5	March	6.73	12.6	0.43	0.63	8.9	50.5	n.d.	30.6	35.3	79.8	31.6	6.8	1.9	31.7	n.d.	n.d.	–	3.9	–	–	–
JS1	March	5.96	15.8	0.45	–	6.5	47.1	n.d.	9.1	5.0	35.6	20.9	7.6	2.7	12.6	0.2	n.d.	–	2.6	–	–52.1	–7.4
KJ1	March	6.87	15.0	0.62	0.37	9.3	87.4	n.d.	87.5	7.4	47.5	23.7	9.8	2.7	54.1	n.d.	n.d.	–	2.2	–	–51.8	–7.3
KJ2	March	6.45	15.7	0.09	–	9.6	10.8	n.d.	7.2	0.9	27.8	8.8	1.2	0.9	5.4	n.d.	n.d.	–	0.7	–	–53.4	–7.6
MK1	March	5.85	14.0	0.59	–	0.6	92.1	n.d.	111.0	20.4	14.5	34.3	11.5	3.7	43.5	n.d.	n.d.	–	2.0	–	–56.1	–7.5
MK2	March	5.96	15.3	0.45	–	1.8	55.7	n.d.	50.2	40.6	34.8	36.2	8.4	2.1	23.1	n.d.	n.d.	–	2.2	–	–50.9	–6.6
MK2	July	5.97	15.2	0.46	–	1.7	55.0	n.d.	52.0	42.0	35.2	37.3	9.2	2.5	24.5	n.d.	n.d.	–	2.3	–16.9	–	–
MK3	March	6.90	12.7	0.16	–	11.1	24.6	n.d.	9.1	1.4	52.2	10.9	2.6	1.3	8.1	n.d.	n.d.	–	1.2	–	–50.0	–6.5
MK4	March	7.73	15.6	0.27	–	5.6	37.7	n.d.	9.5	4.8	102.0	10.3	9.6	2.0	28.5	n.d.	n.d.	–	2.2	–	–56.6	–7.4
MK5	March	7.61	15.2	0.36	–	6.0	50.7	n.d.	13.9	9.2	80.7	12.3	14.5	2.7	38.6	n.d.	n.d.	–	2.3	–	–56.7	–7.4
SD1	March	5.70	15.1	0.33	–	4.8	60.4	n.d.	19.3	6.3	26.2	21.4	9.8	2.6	14.9	n.d.	n.d.	–	2.3	–	–50.5	–7.2
SD3	March	6.43	14.8	0.87	0.42	1.5	57.8	n.d.	248.7	51.6	55.5	18.9	25.4	15.2	96.3	n.d.	0.7	–	2.9	–	–55.9	–7.8
SD4	March	6.99	14.3	0.20	0.46	8.6	28.3	n.d.	12.6	1.6	52.4	10.6	5.1	1.2	16.3	n.d.	n.d.	–	1.4	–	–53.1	–7.5
SD4	July	6.90	14.3	0.25	0.46	8.5	29.0	n.d.	14.0	1.8	53.4	13.0	4.9	2.5	15.3	n.d.	n.d.	–	1.9	–17.7	–	–
D1	March	7.16	14.5	1.07	0.13	3.1	199.1	0.6	n.d.	14.8	255.0	154.2	27.8	18.1	26.0	0.7	0.2	–	6.8	–	–	–
D1	July	7.16	16.9	1.06	0.17	5.8	186.1	0.6	n.d.	12.5	313.6	161.8	14.0	13.8	28.7	0.5	0.2	92.5	10.4	–	–	–

Table 1. (continued).

Well	Month	pH	T (°C)	EC (mS/cm)	Eh (V)	DO (mg/l)	Cl⁻ (mg/l)	Br⁻ (mg/l)	NO₃⁻ (mg/l)	SO₄²⁻ (mg/l)	HCO₃⁻ (mg/l)	Na⁺ (mg/l)	Mg²⁺ (mg/l)	K⁺ (mg/l)	Ca²⁺ (mg/l)	Fe²⁺ (mg/l)	Mn²⁺ (mg/l)	I⁻ (µg/l)	TOC (mg/l)	δ¹³C (‰)	δD (‰)	δ¹⁸O (‰)
D2	March	6.78	14.4	2.83	0.09	1.4	788.2	2.7	n.d.	120.4	377.0	234.3	158.3	57.2	69.2	18.9	2.2	–	8.6	–	–	–
	July	6.96	14.4	2.95	0.07	0.4	842.6	2.4	n.d.	108.5	163.7	234.2	143.0	52.7	63.5	19.1	2.1	63.1	8.1	–	–	–
D3	March	7.03	14.6	3.60	0.12	3.2	973.6	3.4	1.4	135.9	230.1	366.3	125.0	38.4	81.0	8.1	1.3	–	10.2	–	–	–
	July	6.94	14.8	3.38	0.04	2.0	909.4	3.3	n.d.	125.7	331.8	369.0	117.0	39.2	73.7	7.4	1.3	60.8	13.9	−16.1	−35.4	−5.3
D4	March	6.68	14.8	0.45	0.14	3.6	84.7	n.d.	n.d.	19.3	124.8	45.6	15.7	11.2	25.8	4.0	0.7	–	7.9	–	–	–
	July	6.92	17.2	0.68	0.14	7.4	107.9	0.3	n.d.	19.8	226.3	41.8	20.0	13.6	30.3	1.8	0.6	27.0	8.9	–	–	–
D5	March	6.73	15.1	0.27	0.09	4.2	36.6	n.d.	n.d.	20.8	87.2	31.5	6.1	6.5	19.3	4.5	0.3	–	15.1	–	–	–
D7	March	7.02	14.2	3.18	0.08	4.0	806.2	2.9	n.d.	147.2	211.7	417.7	51.5	32.5	27.2	9.6	0.8	–	9.5	–	–	–
	July	7.00	14.8	3.35	0.12	2.3	749.4	2.8	n.d.	142.4	237.8	528.5	49.1	25.9	19.4	8.2	0.9	73.2	11.2	−15.8	−34.6	−5.1
D8	March	7.04	15.7	3.51	0.12	3.2	890.5	3.2	n.d.	115.8	268.6	439.6	55.9	33.0	36.0	6.0	0.5	–	10.3	–	–	–
	July	7.06	14.6	3.34	0.11	2.3	771.0	2.9	n.d.	103.6	301.1	564.0	38.7	22.2	24.1	5.8	0.5	108.5	11.4	–	–	–
D9	March	6.59	14.8	1.98	0.12	1.5	406.0	1.4	n.d.	29.6	339.9	286.7	20.4	20.2	15.7	1.6	0.2	–	11.3	–	–	–
	July	7.38	14.7	1.93	0.13	4.8	396.7	1.4	n.d.	31.8	305.2	364.3	21.3	15.6	12.4	1.9	0.2	91.3	14.0	–	–	–
D11	March	7.24	14.5	1.04	0.13	4.0	196.4	0.6	n.d.	2.2	250.7	104.0	21.1	19.9	12.8	4.1	0.3	–	8.8	–	–	–
	July	7.32	14.5	1.03	0.09	1.8	192.3	0.6	n.d.	1.6	313.7	163.4	16.8	16.1	9.8	2.9	0.2	50.8	8.6	−17.0	−40.0	−5.8
D13	March	7.34	16.6	5.17	0.05	2.6	2145.3	6.9	n.d.	250.2	164.3	734.5	154.7	61.1	91.0	32.5	4.2	–	18.1	–	–	–
	July	6.55	14.5	7.37	0.11	0.9	2306.0	7.9	n.d.	252.9	202.6	856.2	144.5	44.6	94.5	37.3	5.1	122.6	9.2	–	–	–
D14	March	7.55	18.0	3.75	0.09	0.0	1504.8	5.1	n.d.	213.7	114.3	693.4	111.7	53.8	68.7	35.0	4.5	–	23.5	–	–	–
	July	6.55	14.7	6.01	0.14	1.5	1838.9	6.5	0.4	276.7	150.3	789.4	114.5	40.5	68.0	3.2	0.4	59.4	12.6	–	–	–
D17	July	7.32	18.7	1.81	0.12	2.6	435.6	1.4	n.d.	48.9	241.3	370.5	27.0	21.8	15.6	33.0	2.6	72.3	11.9	–	–	–
D18	July	6.65	16.3	1.43	0.11	0.3	430.5	1.3	0.5	59.2	180.6	166.8	45.1	29.9	35.5	25.0	2.7	31.6	9.0	–	–	–
A	July	6.72	14.9	1.41	0.12	1.4	474.9	1.4	n.d.	81.9	135.3	267.7	45.4	31.1	29.9	25.0	2.7	230.4	12.7	−17.7	−38.1	−5.4
B	July	6.98	15.3	3.27	0.13	1.3	1252.9	4.4	n.d.	146.4	289.8	587.7	86.4	29.9	57.2	19.2	3.1	303.7	15.7	−17.5	−39.7	−5.5
C	July	6.79	15.3	10.70	0.13	1.8	3562.6	11.4	n.d.	462.5	218.9	1360.2	208.5	67.5	114.0	69.5	7.0	247.2	8.8	−16.3	−33.6	−4.6
D	July	6.78	14.8	5.06	0.09	1.2	1512.2	5.7	n.d.	267.3	274.3	799.1	86.0	39.3	43.8	15.0	2.1	93.0	12.0	–	–	–

*n.d.: no detection

–: no measurement
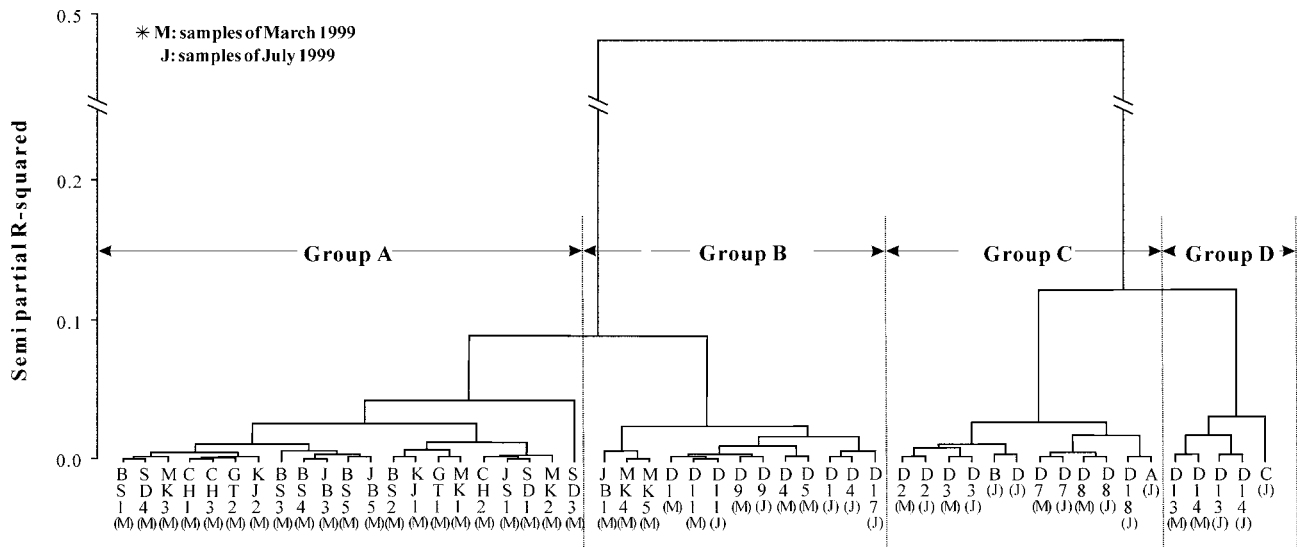
Fig. 2. Dendrogram using Wards method for the samples on March and July, 1999.
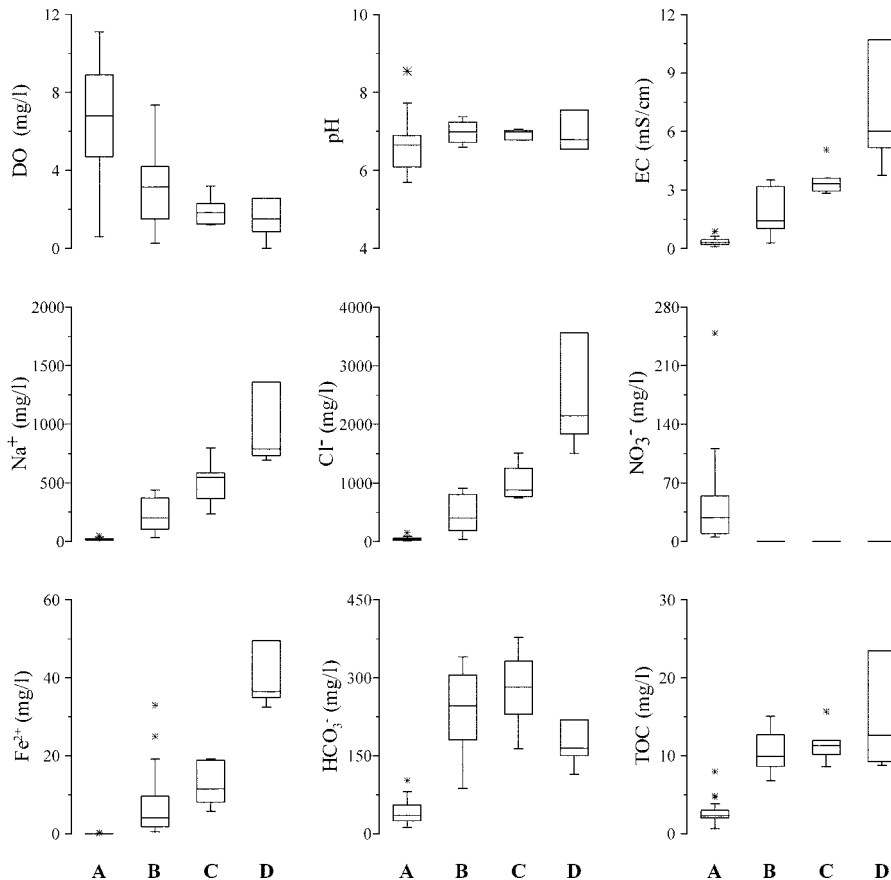
Fig. 3. Box plots of DO, pH, EC, Na^+, Cl^-, NO_3^-, Fe^{2+}, HCO_3^- and TOC for groundwater in groups A, B, C, and D.

groundwaters in group A have high DO (4.7 to 9.7 mg/l) and Eh (0.30 to 0.63 V), implying that the redox condition of groundwaters in group A is an oxic. Under the oxic condition, NH_4^+, the main component of chemical fertilizers, is easily oxidized to NO_3^- due to the nitrification process. During the process, nitrate is enriched and pH is decreased in groundwater (Stumm and Morgan, 1996).

5.2. Groups B, C, and D

5.2.1. Effect of Present Seawater

Among ionic species, Cl^- and Br^- are considered the most conservative. If these ions have the same origin, the Cl^-/Br^- ratio must remain constant (Louvat et al., 1999). Generally, the Cl^-/Br^- ratio of general seawater is between 288 and 292
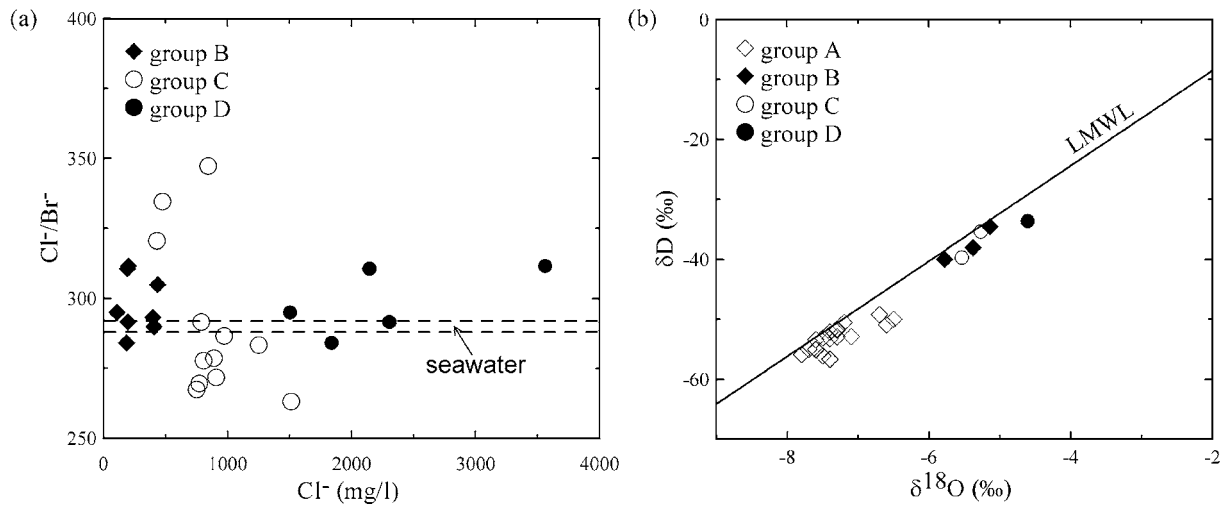
Fig. 4. (a) Plots of Cl⁻/Br⁻ vs Cl⁻ for groundwater in groups B, C, and D. (b) Plots of δD vs δ¹⁸O for groundwater in groups A, B, C, and D (LMWL: $\delta D = 7.94 \pm 0.20\ \delta^{18}O + 8.84 \pm 1.47$; Lee et al., 1999).

(Morris and Riley, 1966; Davis et al., 1998). In Figure 4a, the Cl⁻/Br⁻ ratios of groundwaters in groups B, C, and D range from 263 to 345, showing that these groups are strongly affected by seawater.

Considering the stable isotope compositions of δD and δ¹⁸O for groundwater in the study area, groundwater comprises two groups (Fig. 4b). These indicate that the origin of the two groups is very different. The one including groups B, C, and D have higher δD and δ¹⁸O than the other containing group A. Generally, saline groundwater affected by seawater has a high value for δD and δ¹⁸O, and fresh groundwater is typically iso-topically lighter (Richter et al., 1993). Therefore, groups B, C and D have a mixed origin of seawater and fresh groundwater, while group A has a fresh groundwater origin from meteoric water.
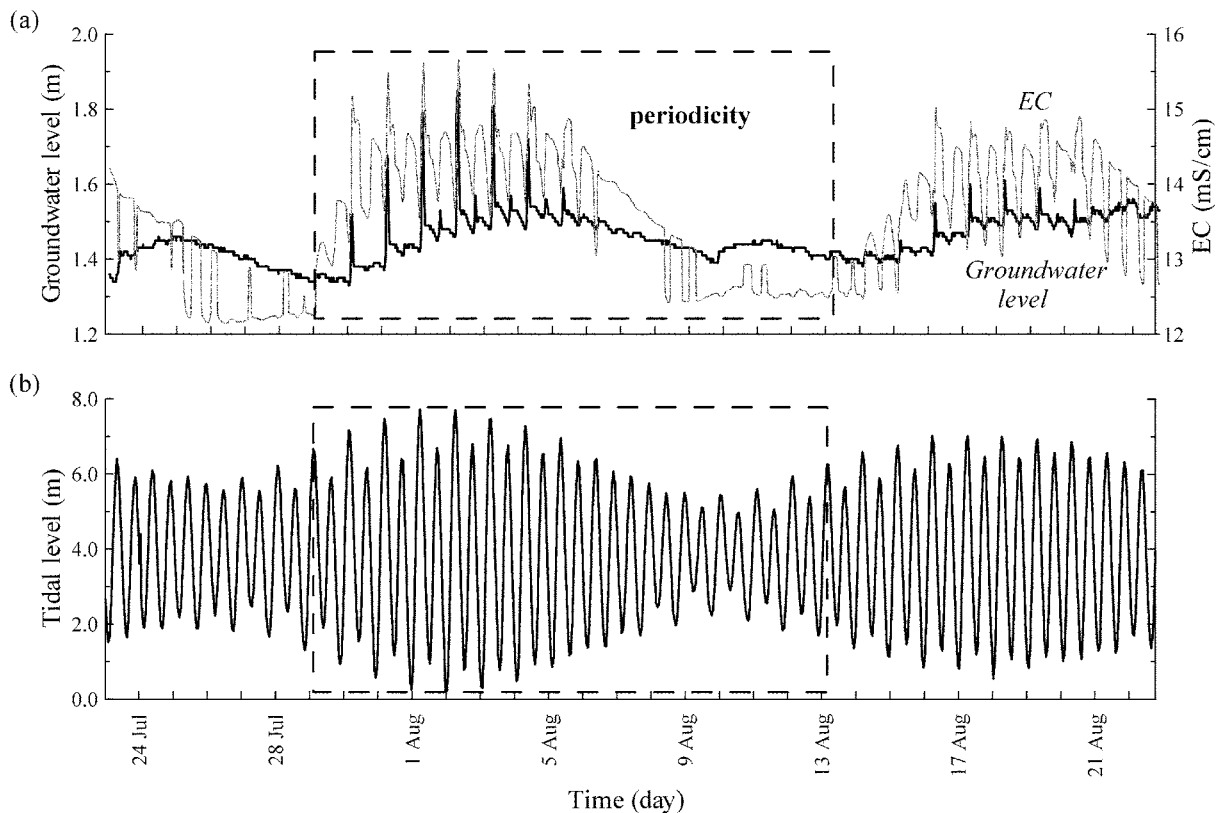
Fig. 5. Monitoring results of EC and groundwater level at the depth of 23m, and measured tidal level from July 23 to August 22, 2000 (data from the National Oceanographic Research Institute).

Fig. 6. Box plots of I^- and $I^-/Cl^- \times 10^6$ for groundwater in groups B, C, and D.

Inspecting the patterns of EC and groundwater level fluctuation at the depth of 23 m (Fig. 5), they have changed repeatedly with two periodicities. One is relatively long term about 15-day and the other is about 0.5-day, which are similar to the periodicities of the tidal level change. These indicate that the groundwater quality is strongly affected by the present seawater causing the tidal level change intruded through the coarse sand layer. In addition, the tidal effect on the groundwater quality can differ according to the tidal level. In the study area, tidal level should overcome its minimum value to cause the change of groundwater quality. In the case of groundwater level, it does not fluctuate but has near constant in a day when tidal level is below 6.3 m. Thus, this tidal level seems to be a minimum value to change the groundwater level. However, in the case of EC, it seems to have no minimum value because EC fluctuates in a day regardless of tidal level. Although tidal level has receded during neap period, the saline effect at the zone, which is close to the freshwater-seawater interface at the coastal, could still be experienced by the groundwater and eventually EC fluctuated (Abdullah et. al, 1997).

5.2.2. Effect of Trapped Old Seawater

Groundwaters in groups B, C, and D have higher iodide concentration than seawater. Also, the I^-/Cl^- ratios are about 1–2 order of magnitude larger in these groundwater than in seawater (10^{-5} to 10^{-6}), and their median values tend to decrease in following the sequence: Group B>C>D (Fig. 6). These suggest that groups B, C, and D groundwaters are affected not only by present seawater but also by trapped old seawater because I^-/Cl^- ratios increase the result of prolonged contact with trapped old seawater (Sukhija et al., 1996). The reclamation area had contained large amounts of seawater trapped in the tideland and sediment containing oxic/anoxic microbes. As the organic matter decomposed after many years, iodide was subject to release and diagenetic redistribution (Price and Calvert, 1977). However, the effect of present seawater is stronger and more direct than the trapped old seawater close to the coastline. Thus, I^-/Cl^- ratios become gradually decreased.

5.2.3. Reduction Processes

Inferred from the enriched nitrate concentration by chemical fertilizers in group A, nitrate concentration is expected to have a high value through the groundwater flow path from group A to group D. In reality, however, the nitrate concentration became gradually lowered through the groundwater flow path, and in groups C and D it was below the detection limit. Also, most groundwaters in groups B, C and D have low DO (0.0 to 4.2 mg/l) and Eh (0.04 to 0.14 V). These are implied that the redox conditions of groundwater change from an oxic into a suboxic/anoxic through the groundwater flow path. Accordingly, the nitrification process also has changed to the reduction processes such as the denitrification, and Fe and Mn reduction processes. As a result, the NO_3^- concentration is gradually decreases through the flow path, while the concentration of Fe and Mn is enriched.

Carbon isotope ratios ($\delta^{13}C$) of dissolved inorganic carbon (DIC) are usually used as a monitoring tool to determine reduction processes (Aggarwal et al., 1997; Landmeyer et al., 1996). In the study area, the composition of $\delta^{13}C$ shows similar values for the four groups (Fig. 7). These results indicate that
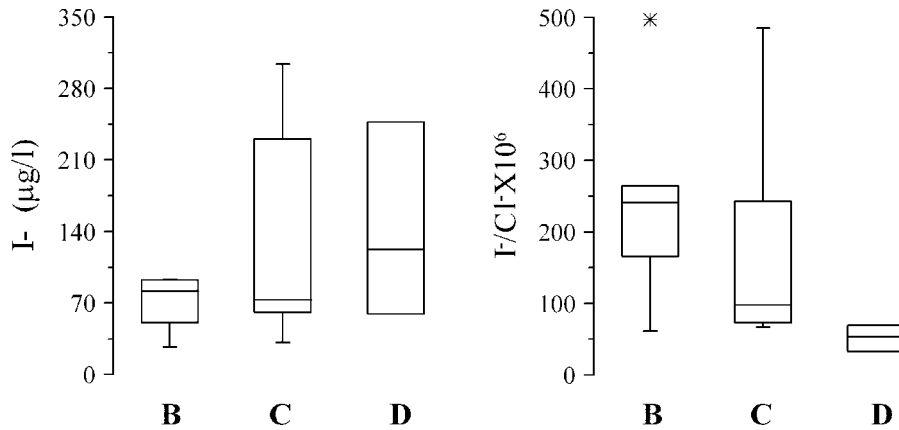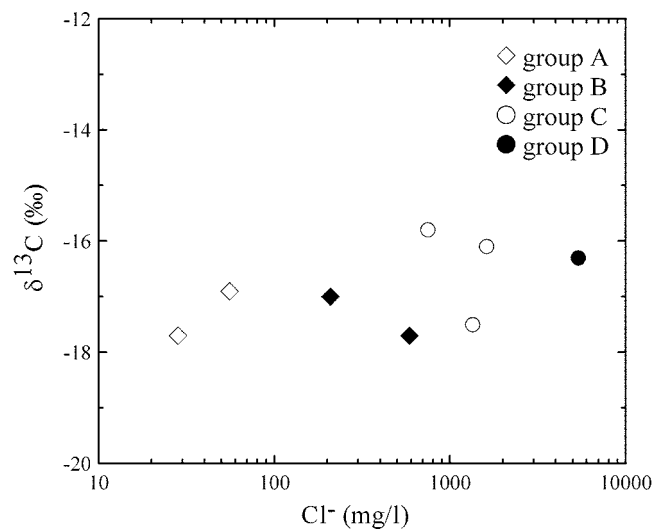

Fig. 7. Plots of $\delta^{13}C$ vs Cl^- for groundwater in groups A, B, C, and D.

δ^{13}C in groups B, C, and D groundwater enrich ^{12}C by means of another source, which is likely to be related to reduction processes. When reduction processes occur, the CO_2 pressure increases as a by-product of microbial respiration, which in turn increases alkalinity and decreases δ^{13}C. Actually, Figure 3 shows that groups B, C, and D groundwaters have a higher TOC and alkalinity concentration than group A. Therefore, carbon isotope composition provides further distinctive evidence for the occurrence of reduction processes in the coastal area.

6. SUMMARY AND CONCLUSIONS

From physico-chemical compositions of groundwaters and their cluster analysis, groundwater in the study area is classified into four groups (A, B, C, and D) and mainly affected by three factors seawater intrusion, chemical fertilizer and reduction processes. Groundwater is recharged inland area and it flows from the inland area to the coastal area through the coarse sand layer with following paths; Group A→B→C→D. Groundwater in group A has high DO and Eh values, which can be considered as an oxic condition. However, as groundwater flow from the inland area to the coastal area, DO and Eh gradually decreases. This suggests that redox conditions of the groundwater tend to change from an oxic into a suboxic/anoxic through the groundwater flow path. Accordingly, this change can influence the main factor governing the groundwater quality.

The area including group A has been used for the agriculture activities, as a result, chemical fertilizers mainly control the groundwater quality. On the other hand, because the area containing groups B, C, and D contacts the Yellows Sea, seawater intrusion is the main factor to govern the groundwater quality. Additionally, this area has included the reclaimed land with a large amount of trapped old seawater and organic matter, indicating that the reclamation processes importantly influence the groundwater quality in the coastal area. Provided sufficient suboxic/anoxic conditions, reduction processes have occurred in the reclaimed area. Therefore, groundwater in groups B, C, and D is largely affected by the seawater intrusion resulted from not only the present seawater but also the trapped old seawater, and reduction processes. However, the effect of these factors is different through its flow path, due to residence time of the residual and the vicinity of the coastline.

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