Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea

Dong-Chan Koh · Kyung-Seok Ko · Yongje Kim · Seung-Gu Lee · Ho-Wan Chang

Abstract Geochemical processes were identified as controlling factors of groundwater chemistry, including chemical weathering, salinization from seawater and dry sea-salt deposition, nitrate contamination, and rainfall recharge. These geochemical processes were identified using principal component analysis of major element chemistry of groundwater from basaltic aquifers in Jeju Island, South Korea, a volcanic island with intense agricultural activities. The contribution of the geochemical processes to groundwater chemistry was quantified by a simple mass-balance approach. The geochemical effects due to seawater were considered based on Cl contributions, whereas the effects due to natural chemical weathering were based on alkalinity. Nitrogenous fertilizers, and especially the associated nitrification processes, appear to significantly affect groundwater chemistry. A strong correlation was observed between Na, Mg, Ca, SO_4 and Cl, and nitrate concentrations in groundwater. Correspondingly, the total major cations, Cl, and SO_4 in groundwater were assessed to estimate relative effect of N-fertilizer use on groundwater chemistry. Cl originates more from nitrate sources than from seawater, whereas SO_4 originates mostly from rainwater. N-fertilizer use has shown the greatest effect on groundwater chemistry, particularly when nitrate concentrations exceed 6–7 mg/L NO_3–N. Nitrate contamination significantly affects groundwater quality and 18% of groundwater samples have contamination-dominated chemistry.

Resumen Se identificaron los procesos geoquímicos como factores que controlan la química del agua subterránea, incluyendo la meteorización química, la salinizacion del agua de mar y la depositación de sal seca de mar, junto con la contaminación del nitrato y la recarga de lluvia. Estos procesos se identificaron usando el análisis del componente principal, de los elementos químicos mayores del agua subterránea, en los acuíferos basálticos en la Isla de Jeju, Corea del Sur, una isla volcánica con intensas actividades agrícolas. La contribución de los procesos geoquímicos, a la química del agua subterránea, se cuantificó por un método de balance de masa simple. Los efectos geoquímicos debidos al agua de mar fueron considerados con base en las contribuciones de Cl, mientras que los efectos debidos a la meteorización química natural fueron basados en la alcalinidad. Los fertilizantes nitrogenados, y sobre todo los procesos de nitrificación asociados, parecen afectar la química del agua subterránea significativamente. Una correlación fuerte se observó entre Na, Mg, Ca, SO_4 y Cl, y las concentraciones del nitrato en el agua subterránea. Correspondientemente, se evaluaron los cationes mayores totales, Cl, y SO_4 en el agua subterránea, para estimar efecto relativo del uso de fertilizante-N en la química del agua subterránea. El Cl se origina más de las fuentes del nitrato que del agua marina, mientras que el SO_4 se origina principalmente del agua lluvia. El uso de fertilizante-N ha mostrado el más grande efecto en la química del agua subterránea, particularmente cuando las concentraciones del nitrato exceden 6–7 mg/L NO_3–N. La contaminación del nitrato afecta significativamente la calidad del agua subterránea y 18% de muestras del agua subterránea tienen una química dominada por la contaminación.

Résumé Des processus géochimiques ont été identifiés comme des facteurs contrôlant la chimie de l'eau souterraine, et notamment l'érosion chimique, la salinisation causée par l'eau de mer et le dépôt sec du sel de mer, ainsi que la contamination par les nitrates et la recharge par la pluie. Ces processus ont été identifiés en utilisant l'analyse à composantes principales des éléments majeurs de la composition chimique de l'eau souterraine d'un aquifère basaltique de l'île de Jeju au sud de la Corée, une île volcanique présentant des activités agricoles intenses. La contribution des processus géochimiques dans la composition chimique de l'eau souterraine a été quantifiée par une simple approche de bilan de masse. Les effets géochimiques liés à l'eau de mer ont été identifiés en se basant sur la part du Cl, tandis que les effets associés à

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l'altération chimique naturelle étaient basés sur l'alcalinité. Les engrais azotés et plus particulièrement les processus de nitrification associés, se révèlent affecter très fortement la composition chimique de l'eau souterraine. Une forte corrélation a été observée entre le Na, Mg, Ca, SO_4 et Cl, et les concentrations en nitrate dans l'eau souterraine. En conséquence, les cations majeurs totaux dans l'eau souterraine, Cl et SO_4 ont été évalué pour estimer l'effet relatif de l'utilisation d'engrais azoté sur la chimie de l'eau souterraine. Le Cl provient plus des sources de nitrates que de l'eau de mer, alors que le SO_4 provient principalement de la pluie. L'utilisation d'engrais azoté induit l'effet le plus important sur la composition chimique de l'eau souterraine, particulièrement quand les concentrations en nitrate dépassent 6–7 mg/L de NO_3–N. La contamination par les nitrates affecte significativement la qualité de l'eau souterraine et 18% des échantillons d'eau souterraine présentent une chimie dominée par cette contamination.

Keywords Hydrochemistry · Groundwater statistics · Contamination · Agriculture · Volcanic island

Introduction

Groundwater may undergo a variety of inorganic chemical reactions as it moves through an aquifer and interacts with the solid framework materials and associated gases. Recharge water sources such as direct precipitation, streamflow, or stormwater runoff, are generally lower in overall constituent concentrations than the underlying groundwater. As groundwater flows downgradient from recharge areas, it commonly becomes more saline and contains various chemical compositions (Runnells 1993). In sparsely populated areas, the quality of shallow groundwater is partly affected by recharge from direct precipitation and local human activities. For deeper groundwater, the predominant effect on groundwater quality is the subsurface physical matrix with which groundwater comes in contact (Bricker and Garrels 1967).

Human input can overwhelm the chemical signature from water–rock interactions, or natural mineralization. Pacheco and Van der Weijden (1996) first quantified the contribution of water–rock interaction on groundwater chemistry which was affected by significant human influence (Fundão, central Portugal), and Pacheco (1998) found that in about 25–30% of the area, shallow groundwater had contamination-dominated chemistries. Pacheco and Szocs (2006), working with shallow groundwater from loess sediments (southwestern Hungary), also concluded that contamination by domestic effluents and farmland fertilizers controls the chemistry of approximately 40% of the water samples. Diffuse contamination has endangered groundwater resources during the last several decades (van den Brink and Zaadnoordijk 1995), as well as point sources such as landfills, waste piles, and storage tanks (Bedient et al. 1994). Diffuse sources of contamination include various land-use practices (Eckhardt and Stackelberg 1995; Grande et al. 1996).

Groundwater beneath Jeju Island is nearly the sole source of potable water. However, recent investigations show that significant nitrate contamination of groundwater has occurred in the coastal area (Oh and Hyun 1997; Woo et al. 2001; Koh et al. 2005), and seawater effects, including intrusion and dry sea-salt deposition, have degraded groundwater quality in the eastern coastal area (Kim et al. 2003). Correspondingly, the groundwater chemistry exhibits the effect of various natural and human processes occurring on the island. This study assessed major geochemical processes and major element chemistry of groundwater in Jeju Island using bivariate comparisons and principal component analysis. Additionally, the relative contribution of each process to dissolved solutes in groundwater was quantified by a mass-balance approach using sequential separation of the effects of the geochemical processes.

Study area

Jeju Island is a volcanic island formed by basaltic and trachytic volcanism from the Pliocene to the Quaternary Period (Won 1976). The island is not presently volcanically active. Basaltic or trachytic lava flows and pyroclastic rocks cover most of the land surface. The basaltic rocks contain interflow structures within a series of lava flows including scoriaceous rocks between lava flows. Because the basaltic rocks are young, and the voids in these structures are not filled, the aquifers composed of basaltic rocks are highly permeable; the aquifers also have a high storage capacity. The Seogwipo Formation, a hydrovolcanic sedimentary formation, underlies the basaltic rocks. This formation contains consolidated or semiconsolidated sedimentary rocks that consist of sand, tuffaceous materials, basaltic rock fragments, and molluscan shells (Sohn et al. 2002). The Seogwipo Formation is not found in the eastern coastal area; however, the formation is distributed in other areas of the island with an average thickness of 100 m (Oh et al. 2000). Most wells are completed at the base of the basaltic rocks or in the upper part of the sedimentary formation.

Jeju Island contains no large industrial facilities, and most land uses are agricultural, including pasture and forest. Agricultural land-use areas are concentrated on the coastal area below 200 m above sea level (asl). Land use in the mountainous areas mainly consists of natural forest and grassland, including pastures (Jejudo 1997).

Methods

Sampling and chemical analysis

Groundwater samples were collected from April to May and from October to December 2002 from 98 public supply wells (Fig. 1) equipped with submersible pumps. Field parameters such as pH, electrical conductivity, temperature, and dissolved oxygen concentration, were measured using a flow-through cell to prevent atmospher-

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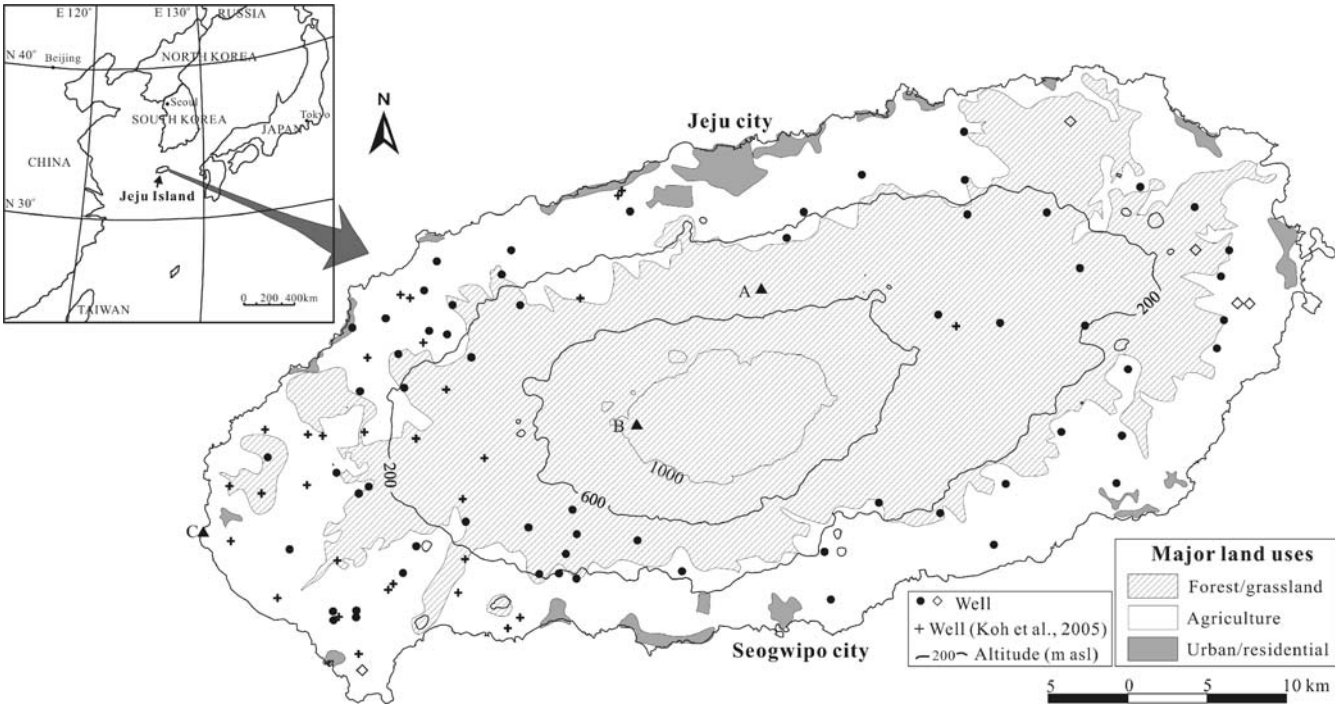

Fig. 1 Location of groundwater sampling sites (*solid circles*) over a land-use map of Jeju Island. Altitudes on the *contour lines* are in meters above sea level. *Diamonds* are the groundwater samples showing effect of salinization by seawater. See text for details. *Crosses* are the sites of Koh et al. (2005), which were considered in this study. *Solid triangles* are the sites of rainwater collection, where *A* and *B* correspond to Kang et al. (1999) and *C* corresponds to Bang et al. (2003). Landuse was classified as forest/grassland, agricultural fields, and urban/residential area based on the map of Jejudo (1997). Two major urban areas of *Jeju city* and *Seogwipo city* are shown. For well numbers, see Fig. 6

ic contact with groundwater. After field parameters stabilized, groundwater samples were field filtered using 0.45-μm pore-sized membrane filters and collected in high-density polyethylene (HDPE) bottles. Samples for cation analyses were acidified with concentrated nitric acid. Cations and silica were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), and anions were analyzed by ion chromatography at the Korea Institute of Geoscience and Mineral Resources. Alkalinity was determined by Gran titration in the field. The cation–anion balance was cross-checked, and for most analytical results, the error was less than 5%. Field parameter results and dissolved element concentrations are summarized in Table 1 for 68 groundwater samples. For the remaining 30 samples, which were collected in April 2002, the hydrogeochemical data were given in Koh et al. (2005) (Fig. 1).

Land-use characteristics

Most wells used for irrigation are located apart from the urban/residential area in agricultural fields used for vegetables, potatoes, and orchards of mandarin oranges (Fig. 1). The impacts of agricultural land use on nitrate contamination of groundwater are not uniform on a regional scale because of variation of intensity of fertilizer use in a nearby area, groundwater age, and recharge altitude for each well (Koh et al. 2005).

The residential area is sparsely populated and has no large sewage-treatment facility. Because the wells used in this study are away from the residential area, the effect of solid wastes or sewage (from septic systems) on groundwater is not large. The area near the landfills and large livestock facilities are not included in this study. Two urban areas, Jeju city and Seogwipo city, located at the center of the northern and southern coasts, respectively, were also excluded.

Multivariate statistical analysis

The groundwater quality data collected from the study area during 2002 were analyzed with a multivariate statistical method to identify major geochemical processes controlling groundwater chemistry. Koh et al. (2005) show that tritium concentration is poorly correlated with the well depth. This result suggests that well depth is a poor indicator for the location of a transmissive zone as related to the pumped water. Furthermore, most wells have multiple screened zones that obscure the difference of total depth of each well. Thus, well depth is not used as a meaningful variable in this study. Principal component analysis was performed for hydrochemical data of 98 groundwater samples to infer the controlling factors of groundwater chemistry. Principal component analysis has been widely applied in the interpretation of hydrogeochemical data (Evans et al. 1996; Cameron 1996; Adams

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Table 1 Field parameters, concentrations of dissolved elements in groundwater samples, and well information

Well No.	Depth (m)	Elv. (m asl)	Collection date	T (°C)	pH	EC (μS/cm)	DO (mg/L)	Ca (meq/L)	Mg (meq/L)	Na (meq/L)	K (meq/L)	HCO_3[a] (meq/L)	Cl (meq/L)	SO_4 (meq/L)	NO_3 (meq/L)	CBE[b] (%)	SiO_2 (mg/L)	Br (mg/L)
1	250	300	23-May-02	18.8	8.7	186	7.0	0.34	0.35	0.89	0.20	1.53	0.22	0.05	0.02	−0.8	34	ND
2	120	80	23-Oct-02	16.0	7.9	165	NM	0.39	0.49	0.71	0.11	0.65	0.71	0.06	0.27	0.3	31	ND
3	143	127	23-Oct-02	15.9	8.5	109	NM	0.35	0.31	0.43	0.09	0.80	0.19	0.04	0.02	5.8	27	ND
5	102	90	23-Oct-02	15.8	7.6	124	NM	0.31	0.47	0.46	0.09	0.67	0.32	0.04	0.15	5.3	31	ND
6	431	511	24-May-02	15.9	7.8	90	9.9	0.22	0.33	0.28	0.08	0.68	0.13	0.03	0.01	3.0	35	ND
7	160	172	23-May-02	17.4	8.8	128	8.4	0.47	0.28	0.47	0.09	0.80	0.25	0.04	0.10	4.7	30	ND
8	180	122	29-Oct-02	15.4	7.1	233	14.6	0.48	0.85	0.75	0.14	0.34	0.65	0.20	0.99	0.9	31	ND
9	88	40	6-Dec-02	15.0	7.2	172	8.9	0.44	0.55	0.59	0.13	0.50	0.51	0.09	0.47	4.0	29	ND
10	200	163	25-Oct-02	15.5	7.8	64	NM	0.17	0.18	0.24	0.05	0.38	0.14	0.03	0.03	4.6	25	ND
11	212	138	24-Oct-02	16.4	8.4	110	NM	0.30	0.31	0.48	0.08	0.69	0.21	0.03	0.10	6.1	28	ND
12	270	230	22-Oct-02	14.5	8.2	90	NM	0.21	0.27	0.33	0.07	0.43	0.24	0.04	0.08	4.2	27	ND
13	290	250	21-Oct-02	14.2	7.9	64	NM	0.12	0.15	0.20	0.05	0.28	0.15	0.04	0.02	4.2	25	ND
15	270	240	25-Oct-02	16.4	8.0	67	NM	0.20	0.16	0.25	0.04	0.40	0.12	0.04	0.04	3.7	24	ND
16	80	47	1-Nov-02	15.5	7.6	175	NM	0.45	0.64	0.58	0.13	0.73	0.43	0.09	0.38	5.0	31	ND
17	220	145	4-Apr-02	14.0	8.0	136	9.2	0.25	0.41	0.60	0.10	0.62	0.33	0.09	0.19	4.6	34	ND
18	150	108	31-Oct-02	15.6	8.1	148	11.1	0.37	0.46	0.54	0.13	0.63	0.35	0.07	0.35	3.6	30	ND
21	180	149	29-Oct-02	15.2	7.7	113	NM	0.26	0.39	0.36	0.09	0.55	0.26	0.04	0.19	2.0	29	ND
22	112	108	6-Dec-02	14.6	7.9	129	10.3	0.29	0.38	0.47	0.09	0.48	0.37	0.07	0.23	2.6	28	ND
23	168	143	30-Oct-02	15.3	7.8	107	9.9	0.22	0.35	0.39	0.09	0.58	0.27	0.04	0.13	1.2	33	ND
24	90	66	30-Oct-02	15.7	7.6	206	10.2	0.50	0.72	0.64	0.13	0.65	0.53	0.12	0.76	−1.9	32	ND
25	70	55	22-Oct-02	15.3	7.8	222	0.0	0.62	0.74	0.72	0.13	0.43	0.62	0.13	0.99	0.9	26	ND
26	215	190	21-Oct-02	14.8	7.6	92	10.8	0.21	0.28	0.33	0.08	0.45	0.22	0.05	0.09	5.4	29	ND
27	200	101	22-Oct-02	16.1	8.6	147	NM	0.36	0.37	0.64	0.13	0.70	0.33	0.07	0.23	5.9	27	ND
31	243	218	31-Oct-02	15.5	7.7	158	9.3	0.33	0.59	0.60	0.14	0.80	0.35	0.08	0.33	3.0	31	ND
32	137	126	31-Oct-02	15.8	7.2	264	8.7	0.65	1.04	0.80	0.18	0.99	0.60	0.15	0.77	3.1	28	ND
35	150	133	30-Oct-02	15.8	7.6	130	NM	0.26	0.46	0.48	0.09	0.69	0.38	0.07	0.16	−0.3	32	ND
36	300	288	29-Oct-02	15.5	8.2	86	9.8	0.17	0.29	0.30	0.08	0.54	0.22	0.04	0.04	−0.7	29	ND
37	99	91	22-Oct-02	15.5	7.9	231	NM	0.29	0.62	1.29	0.11	0.47	1.71	0.21	0.01	−1.9	22	ND
38	88	83	9-Dec-02	15.7	7.9	379	10.3	0.34	0.78	2.67	0.17	0.73	2.68	0.24	0.07	2.8	28	0.49
39	100	56	4-Dec-02	15.3	7.1	139	10.1	0.35	0.43	0.45	0.10	0.45	0.39	0.09	0.37	1.2	27	ND
41	292	265	30-Oct-02	18.2	8.4	136	8.7	0.28	0.39	0.68	0.17	1.04	0.23	0.05	0.04	5.3	29	ND
42	72	58	11-Apr-02	15.6	7.1	86	9.1	0.24	0.26	0.25	0.05	0.33	0.17	0.04	0.21	2.0	29	ND
43	188	179	11-Apr-02	15.3	7.1	86	9.7	0.22	0.25	0.26	0.05	0.32	0.23	0.04	0.15	2.5	28	ND
45	92	45	30-Oct-02	17.3	7.9	211	4.2	0.57	0.53	0.79	0.15	0.91	0.63	0.16	0.27	1.7	25	ND
50	170	153	2-Apr-02	16.7	8.2	114	9.0	0.26	0.39	0.44	0.11	0.76	0.20	0.04	0.07	4.9	40	ND
53	121	89	1-Nov-02	15.3	7.5	200	9.5	0.41	0.68	0.66	0.14	0.55	0.52	0.14	0.58	2.7	32	ND
54	230	205	24-Oct-02	15.3	7.9	124	NM	0.34	0.52	0.40	0.07	0.81	0.24	0.05	0.10	5.1	27	ND
55	280	255	25-Oct-02	15.4	7.6	65	NM	0.19	0.18	0.23	0.04	0.44	0.12	0.03	0.02	2.6	22	ND
58	119	44	5-Apr-02	15.0	9.2	124	7.4	0.50	0.24	0.46	0.09	0.84	0.23	0.06	0.04	4.5	24	ND
59	80	42	8-Dec-02	15.5	7.8	165	7.9	0.50	0.45	0.62	0.14	0.66	0.54	0.11	0.46	−2.0	27	ND
62	214	186	5-Apr-02	14.9	8.3	87	9.2	0.20	0.26	0.30	0.08	0.48	0.19	0.04	0.09	2.0	35	ND
63	200	186	23-May-02	16.8	7.7	117	9.8	0.38	0.35	0.39	0.04	0.71	0.23	0.05	0.11	2.9	30	ND
64	400	416	24-May-02	18.7	8.7	189	8.2	0.39	0.42	0.89	0.17	1.57	0.24	0.04	0.01	0.2	30	ND
67	142	104	31-Oct-02	15.2	7.6	148	9.5	0.38	0.51	0.44	0.09	0.59	0.39	0.08	0.37	−0.1	29	ND
68	160	132	9-Dec-02	15.4	7.2	338	9.3	0.70	0.96	1.51	0.16	0.88	2.05	0.20	0.07	2.0	33	ND
69	100	89	10-Dec-02	15.4	7.3	201	9.9	0.35	0.59	0.87	0.13	0.69	0.82	0.10	0.24	2.4	32	ND
70	95	82	10-Apr-02	16.1	8.0	185	9.1	0.34	0.57	0.80	0.10	0.72	0.70	0.08	0.08	7.0	37	ND
71	80	62	10-Apr-02	15.9	7.8	135	9.2	0.39	0.48	0.42	0.08	0.67	0.27	0.04	0.24	5.8	37	ND
72	170	144	9-Apr-02	15.2	8.1	94	9.1	0.25	0.33	0.32	0.07	0.66	0.17	0.04	0.02	4.5	36	ND

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75	270	252	23-Oct-02	15.7	10.5	160	NM	0.28	0.34	0.36	0.09	0.72	0.22	0.04	0.02	2.7	26	ND
77	120	96	9-Dec-02	15.4	7.9	172	9.9	0.30	0.50	0.70	0.11	0.52	0.57	0.07	0.32	3.9	29	ND
79	135	65	31-Oct-02	16.0	7.2	154	8.4	0.44	0.46	0.50	0.08	0.51	0.36	0.09	0.34	6.2	29	ND
82	170	130	22-Oct-02	14.3	8.1	86	NM	0.20	0.25	0.31	0.06	0.42	0.20	0.05	0.09	4.1	24	ND
83	280	241	22-Oct-02	14.5	8.0	88	NM	0.19	0.25	0.33	0.06	0.42	0.23	0.05	0.07	4.0	24	ND
84	116	37	30-Oct-02	18.0	7.8	242	26.2	0.70	0.65	0.80	0.13	0.90	0.66	0.19	0.44	2.2	24	ND
87	80	62	10-Dec-02	15.9	6.7	442	10.0	0.36	0.92	2.64	0.18	0.67	2.95	0.29	0.10	1.2	28	0.29
88	290	260	30-Oct-02	14.9	8.5	107	8.8	0.22	0.25	0.49	0.13	0.49	0.30	0.04	0.13	5.6	31	ND
90	325	338	9-Apr-02	16.0	7.5	131	8.3	0.33	0.58	0.40	0.08	0.91	0.24	0.04	0.06	5.2	43	ND
92	116	96	24-Oct-02	15.0	8.0	114	NM	0.26	0.36	0.40	0.08	0.79	0.23	0.04	0.08	−1.4	21	ND
94	212	135	1-Nov-02	13.4	8.4	124	4.7	0.31	0.42	0.52	0.07	0.57	0.44	0.07	0.07	6.8	30	ND
96	80	22	8-Dec-02	19.0	8.3	682	1.5	1.10	1.50	3.46	0.28	1.26	4.56	0.39	0.33	−1.6	25	0.52
97	142	113	23-Oct-02	16.0	8.1	156	NM	0.37	0.48	0.64	0.13	0.61	0.51	0.07	0.30	3.9	27	ND
99	107	73	4-Dec-02	15.5	7.2	283	10.9	0.68	1.10	0.77	0.11	0.63	0.79	0.27	1.13	−2.9	30	ND
101	90	55	24-Oct-02	15.3	7.1	110	NM	0.32	0.32	0.33	0.08	0.38	0.26	0.05	0.31	2.2	23	ND
102	420	430	9-Apr-02	14.0	8.4	67	9.0	0.15	0.20	0.23	0.06	0.42	0.14	0.04	0.01	1.5	31	ND
104	410	417	11-Apr-02	14.6	8.9	57	8.4	0.15	0.16	0.17	0.05	0.38	0.11	0.03	0.01	0.4	31	ND
105	270	213	23-May-02	18.4	7.9	125	9.4	0.42	0.35	0.42	0.06	0.87	0.24	0.04	0.03	3.0	37	ND
106	305	342	24-May-02	15.2	8.2	77	10.5	0.16	0.22	0.27	0.07	0.38	0.19	0.06	0.05	3.1	35	ND

NM not measured, *ND* not detected

[a] total alkalinity

[b] *Charge balance error* $(\Sigma\text{cation}-\Sigma\text{anion})/(\Sigma\text{cation}+\Sigma\text{anion})\times 100$

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et al. 2001). Among the available data, 10 variables were chosen: pH, Ca, Mg, Na, K, HCO_3, Cl, SO_4, NO_3, and SiO_2. EC was excluded from the analysis because it is a measure of sum of concentrations of major ions. The factors were extracted from a correlation matrix of the variables by principal component analysis.

Results and discussion

Hydrogeochemical characteristics

Most groundwater beneath Jeju Island is (Na, Mg)-HCO_3 type under alkaline conditions with an average pH of 8.0. Also, high dissolved oxygen (DO) concentrations are present with an average concentration of 8.3 mg/L (Table 1). Mg concentrations are distinctively higher in groundwater in the basaltic aquifers beneath Jeju Island as compared to groundwater in the crystalline basement of granites and gneisses. This result is common in mainland South Korea (Jeong 2001).

Comparison of Na and SO_4 with Cl concentrations shows that groundwater salinization is evident in five samples (Fig. 2a and b; five samples constitute a small portion of the total number of samples). These samples are located in the eastern coastal area with the exception of one sample taken from well 96 located in the southwestern coastal area (see Fig. 1). These samples are also distinguished in the comparison of Na and SO_4 with NO_3 from the other samples (Fig. 2c and d). Three samples of the groundwater affected by salinization have detectable Br (Table 1). Kim et al. (2003) showed that groundwater salinization was occurring in the eastern coastal area and the source of salinity was modern seawater.

To assess the effect of nitrate contamination sources on groundwater quality, the samples with nitrate concentrations less than 1 mg/L NO_3–N, excluding the five samples with a discernible effect of seawater, are assumed to be unaffected by nitrate sources and designated as non-contaminated water (Hallberg and Keeney 1993). The remaining samples are regarded as nitrate-contaminated water. Many samples exceed the nitrate drinking-water standard for South Korea of 10 mg/L NO_3–N. In some samples, nitrate is a predominant anion (Table 1). This result suggests that the sources of nitrate contamination strongly affect groundwater chemistry. Furthermore, Na and SO_4 concentrations show positive correlations with nitrate concentrations; these correlations suggest an effect

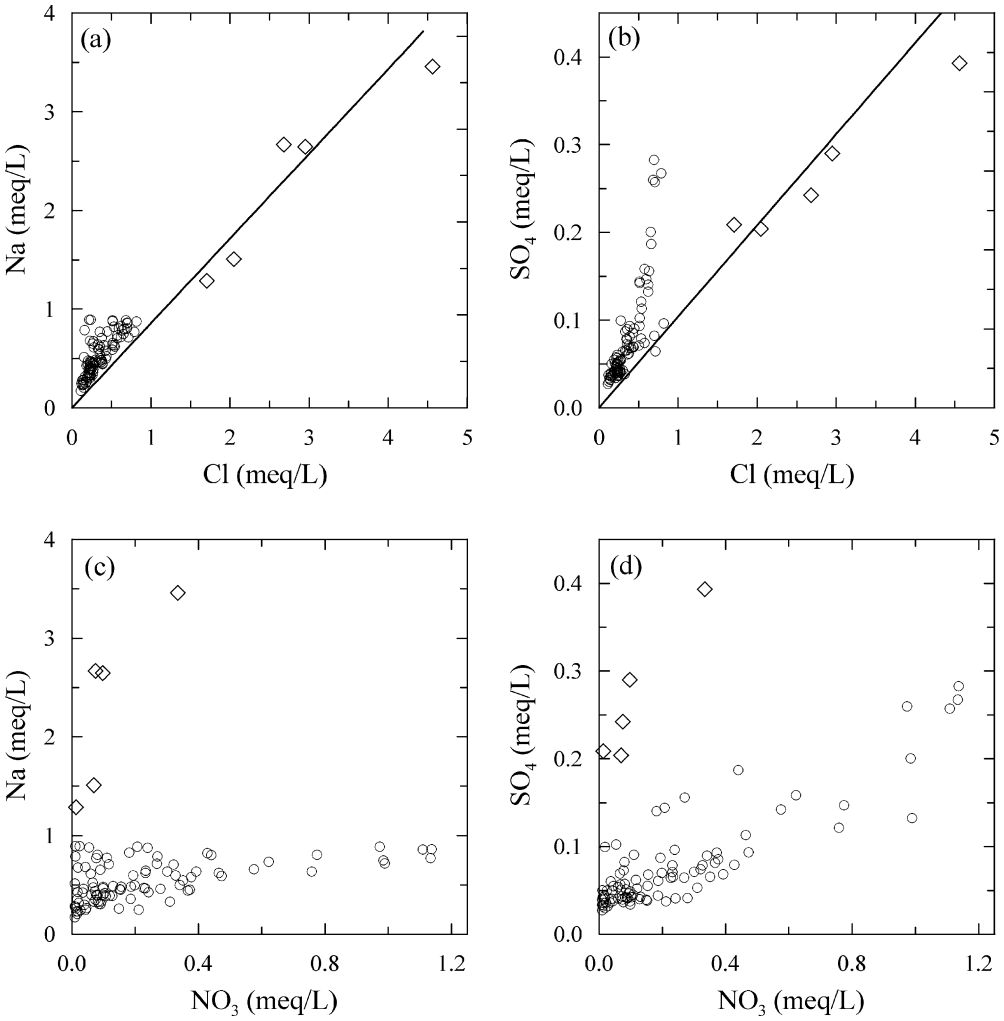

Fig. 2 Bivariate plots. **a** Na vs. Cl and **b** SO_4 vs. Cl. *Solid lines* are seawater dilution lines. **c** Na vs. NO_3, **d** SO_4 vs. NO_3. Groundwater that is distinctively affected by salinization is indicated separately as *diamonds*

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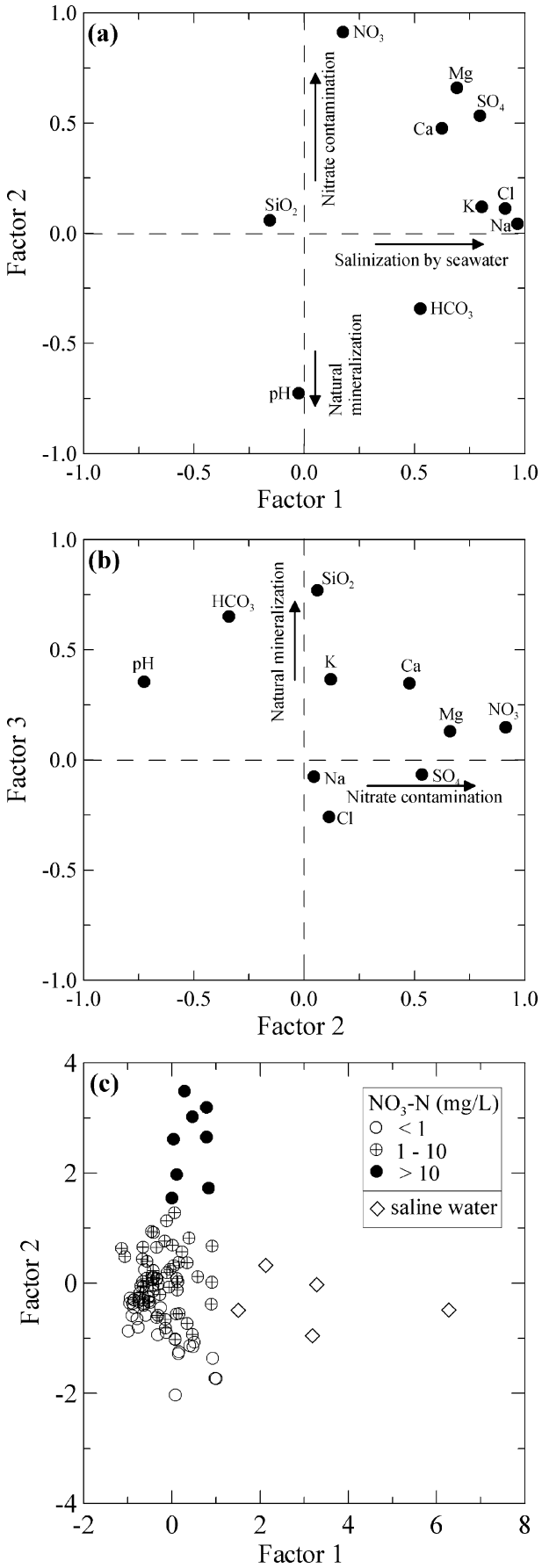

◀ **Fig. 3** Factor loading diagrams for variables, **a** factor 1 vs. factor 2, **b** factor 2 vs. factor 3, and a factor score diagram for samples, **c** factor 1 vs. factor 2

on groundwater chemistry related to the nitrate contamination. This effect includes increased chemical weathering, as well as direct inputs from the dissolution of fertilizers containing Na and SO_4 (Fig. 2c and d).

Chemical weathering by N-fertilizer use

Because agricultural land use is predominant at most well locations, the contamination sources of groundwater are chemical fertilizers and manures used for cultivated lands. Song et al. (1999) reported nitrate-$\delta^{15}N_{AIR}$ of +4 to +7 (avg. +5.2), which was reported in per mil (‰) relative to N_2 in atmospheric air for groundwater from 11 wells located in coastal areas around Jeju Island with agricultural land usage. These concentrations are much lower than nitrate-$\delta^{15}N_{AIR}$ concentrations for manures of pigs and chickens (+13 to +15‰). This result is indicative of the strong effect of chemical fertilizers (−0.2 to +1.3‰) on nitrate contamination of groundwater.

Fertilizer application practices utilizing ammonium or urea sources can result in soil acidification due to the release of protons during nitrification. Specifically, oxidation of these forms of nitrogenous fertilizers generates acidity during bacterial nitrification (Ehrlich 1990) and is given as

$$\begin{aligned} &NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O1/2(NH_2)_2CO \\ &\quad + 2O_2 \rightarrow NO_3^- + 3/2H^+ + 1/2HCO_3^-, \\ &\text{with urea hydrolysis } \left[1/2(NH_2)_2CO + H_2O \rightarrow NH_4^+ + 1/2CO_3^{2-}\right] \end{aligned} \quad (1)$$

The chemical reaction described in Eq. (1) can cause clay mineral degradation and reduced mineral cation exchange capacity (McGahan et al. 2003). Collins and Jenkins (1996) suggested that acidity related to N-fertilizer

Table 2 Varimax rotated principal-component factor loadings

Variables	F1	F2	F3	Communalities[a]
pH		(−0.73)		0.654
Ca	(0.62)	(0.48)		0.736
Mg	(0.69)	(0.66)		0.932
Na	0.97			0.940
K	0.80			0.795
HCO_3	(0.52)		(0.65)	0.816
Cl	0.91			0.909
SO_4	0.80	(0.53)		0.923
NO_3		0.91		0.887
SiO_2			0.77	0.621
Eigenvalue (λ)	4.24	2.46	1.51	
% variance explained	42.4	24.6	15.1	
Cumulative % variance explained	42.4	67.0	82.1	

Loadings in range 0.40–0.75 are given in parentheses, loadings less than 0.40 are not shown.

[a] Communalities were calculated using all of three factor loadings

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Table 3 Rainwater compositions measured for wet deposition in Jeju Island (mg/L)

Sites	Ca	Mg	Na	K	Cl	SO_4	NO_3	Period	Ref.
A	0.20	0.17	1.65	0.22	2.57	2.02	1.12	1997–1998	Kang et al. (1999)
B	0.12	0.10	0.93	0.14	1.44	1.66	0.82	1997–1998	Kang et al. (1999)
C	0.52	0.29	1.55	0.20	2.35	2.09	1.17	1999–2001	Bang et al. (2003)
Mean	0.28	0.19	1.37	0.19	2.12	1.92	1.03		

application is buffered by land-tillage practices that promote increased weathering and correspondingly higher base cation concentrations. The clay mineral degradation and reduced cation exchange capacity that stems from nitrification processes likely contribute to a significant portion of the total major cation concentration. The soil acidity also appears to be transferred to underlying basaltic rocks. The soil is 0.6 m thick, on average, and less than 1 m thick for 85% of the total area of Jeju Island (Jejudo 1997). Therefore, the acidity generated from N-fertilizer application likely exceeds the buffering capacity of the soil. Furthermore, groundwater recharge occurring during the rainy season from June to September facilitates nitrate transport to the water table (Lee et al. 1999). Thus, it can be assumed that the geochemical processes associated with N-fertilizer use and the corresponding chemical weathering of basaltic rocks, dominate over natural weathering processes involving CO_2 in Jeju Island. This weathering can account for an increase in cation concentrations along with increasing nitrate concentrations.

Identification of hydrogeochemical processes

Principal component analysis of groundwater chemistry data shows that three factors explain much of the variance (Table 2). The factors with Eigen values larger than 1 were selected and rotated iteratively by the Varimax method (Davis 1986), which maximizes the variance of the factor. For factor loadings, a high loading was defined as greater than 0.75, and a moderate loading was defined as 0.40–0.75. Loadings of less than 0.4 were considered insignificant (Evans et al. 1996). Factor 1 has high or moderate loadings for most variables, especially Na and Cl; whereas

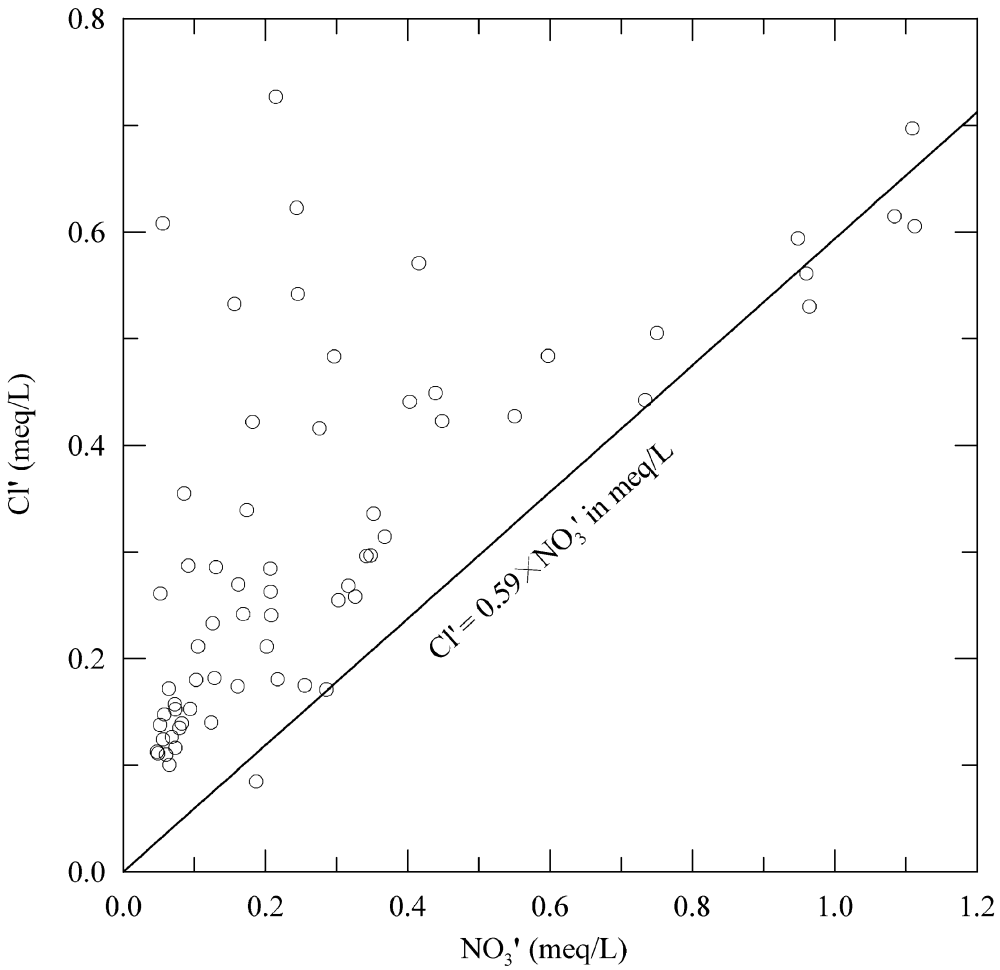

Fig. 4 Cl vs. NO_3 in concentration (meq/L) corrected for rainwater contribution

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this factor has insignificant loadings for NO_3 and SiO_2. Factor 1 loadings indicate groundwater salinization by seawater. Factor 2 appears related to nitrate contamination as the NO_3 loading is distinctively higher than the loadings for other variables. Moderate loading for SO_4 corresponds to the correlation between measured NO_3 and SO_4 concentrations, and the negative loading for pH shows the effect of acid generation due to nitrification processes. Factor 3 has the simplest loading structure; factor 3 has a high SiO_2 loading and a moderate HCO_3 loading. This factor appears to be related to natural mineralization processes that are accompanied by increased alkalinity and SiO_2. The plots of factor loadings (Fig. 3a and b) illustrate these three factors. Figure 3a shows seawater salinization and nitrate contamination and Fig. 3b indicates natural mineralization on a larger scale. Factor scores for each sample also show these geochemical processes (Fig. 3c). Saline water, non-contaminated water, and nitrate-contaminated water are well distinguished in Fig. 3c, which shows samples with the higher nitrate concentrations associated with factor 2. The major geochemical processes were identified using bivariate comparisons, principal component analysis of field parameters, and major element concentrations. Considering the coastal setting of the study area, the sea-salt deposition effects may be significant. This effect was incorporated into salinization by seawater, or factor 1, and is discussed in the following section. Based on the above methods, four major geochemical processes were determined to control groundwater chemistry in the study area, including: (1) rainwater recharge, (2) seawater and sea-salt deposition, (3) chemical weathering by CO_2, and (4) nitrate contamination.

Geochemical mass balance

The geochemical mass balance was first introduced and demonstrated by Garrels and Mackenzie (1967) to interpret evolution of spring water chemistry with reactions of primary silicate minerals with CO_2-charged rainwater producing dissolved constituents and clay minerals. A similar approach was applied to quantify the contribution of major geochemical processes to groundwater chemistry identified by the statistical analyses of hydrogeochemical data. In this study, the mass balance was focused on separation of various geochemical processes, as well as natural mineralization and quantification of impact of human input, which corresponds

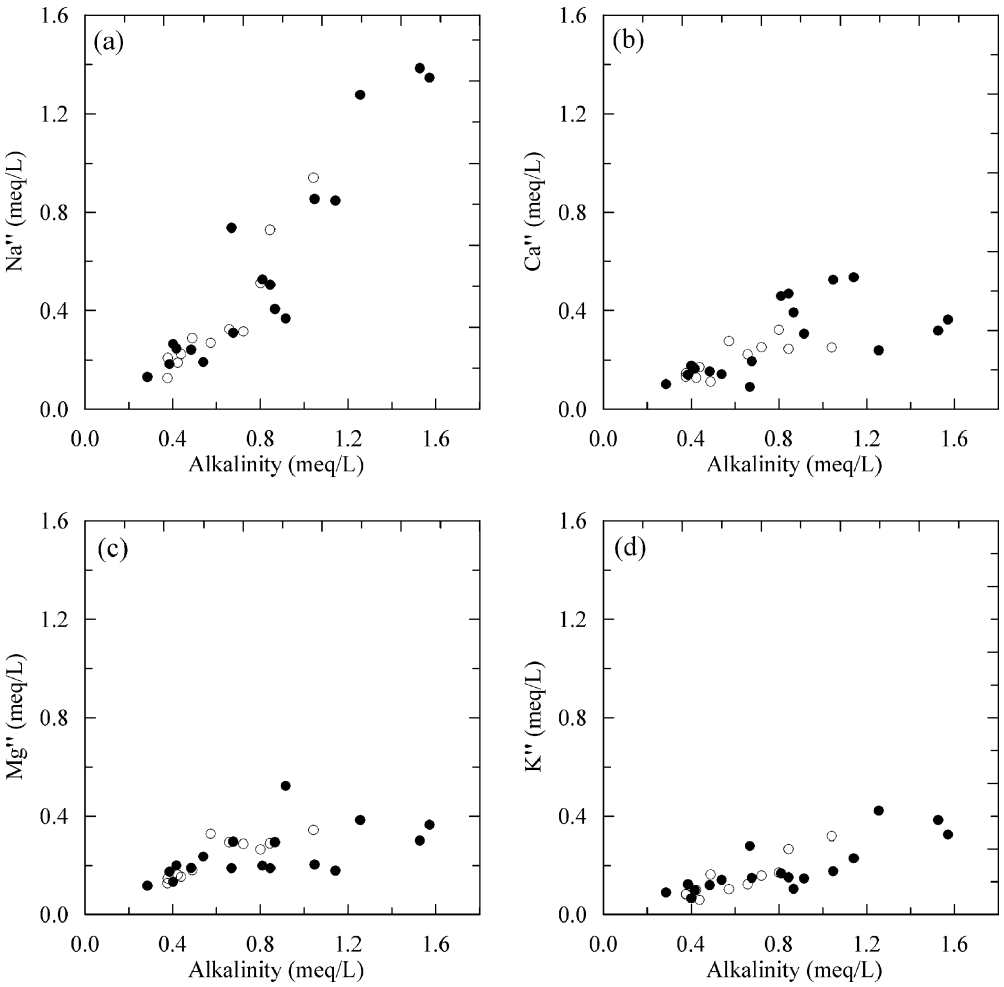

Fig. 5 Cation concentrations corrected for rainwater and seawater contributions vs. total alkalinity as HCO_3 in meq/L for non-contaminated water. *Open circles* represent basaltic rocks and *solid circles* represent trachytic rocks

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mainly to agricultural activities on cultivated area. For the processes where major ions do not undergo ion exchange or precipitation, these processes are considered conservative. Solid phase precipitation processes are not probable for groundwater underlying the study area. Thus, the contribution of each geochemical process can be separated by sequential subtraction of the measured ion concentrations representative of each process. The approach used to determine the relative contribution of each process is described below.

Contribution of rainwater and seawater

The contribution of groundwater recharge to dissolved solutes can be estimated from rainwater chemistry and evapotranspiration (Appelo and Postma 1994). The chemistry of rainwater was investigated for wet deposition only in some studies of Jeju Island (Kang et al. 1999; Bang et al. 2003). These chemical compositions are listed in Table 3 (see also Fig. 1 for rainwater collection locations). Although the effect of sea-salt deposition, or aerosols derived from seawater, decreases toward the center of the island, rainfall chemistry was determined as an average of the results of three studies because the data are insufficient for defining the relation between the sea-salt deposition effect and the distance from the coast. Evapotranspiration was estimated as 33.7% of precipitation by a daily soil-moisture balance model (Jejudo 2003) based on meteorological data from coastal stations. These data may overestimate the evapotranspiration for the mountainous area. The contribution of rainfall derived recharge to dissolved solutes was subtracted from measured ion concentrations in groundwater by considering rainwater chemistry and evapotranspiration, which was used for recharge estimation via the chloride method in a vegetated area where surface runoff is negligible (Sharma and Hughes 1985) and is given as:

$$C_{\mathrm{i}}' = C_{\mathrm{i}} - \frac{C_{\mathrm{i}}^{rw}}{1-E}, \tag{2}$$

where

C_{i}' concentration of ion i corrected for rainwater contribution
C_{i} measured concentration of ion i in groundwater
C_{i}^{rw} estimated mean concentration of ion i in rainwater
E evapotranspiration, % in precipitation

Increased groundwater salinity in the eastern coastal area has been previously identified (Kim et al. 2003). The upconing of saltwater with pumping is unlikely because transmissivity of the basaltic aquifers is large compared to the pumping rate in the eastern coastal area (Jejudo 2003). In other coastal areas, groundwater salinity is not discernible, and appears to be unrelated to the distance from seawater.

Groundwater can be affected by dry deposition of sea-salt aerosols, as well as a direct contact between

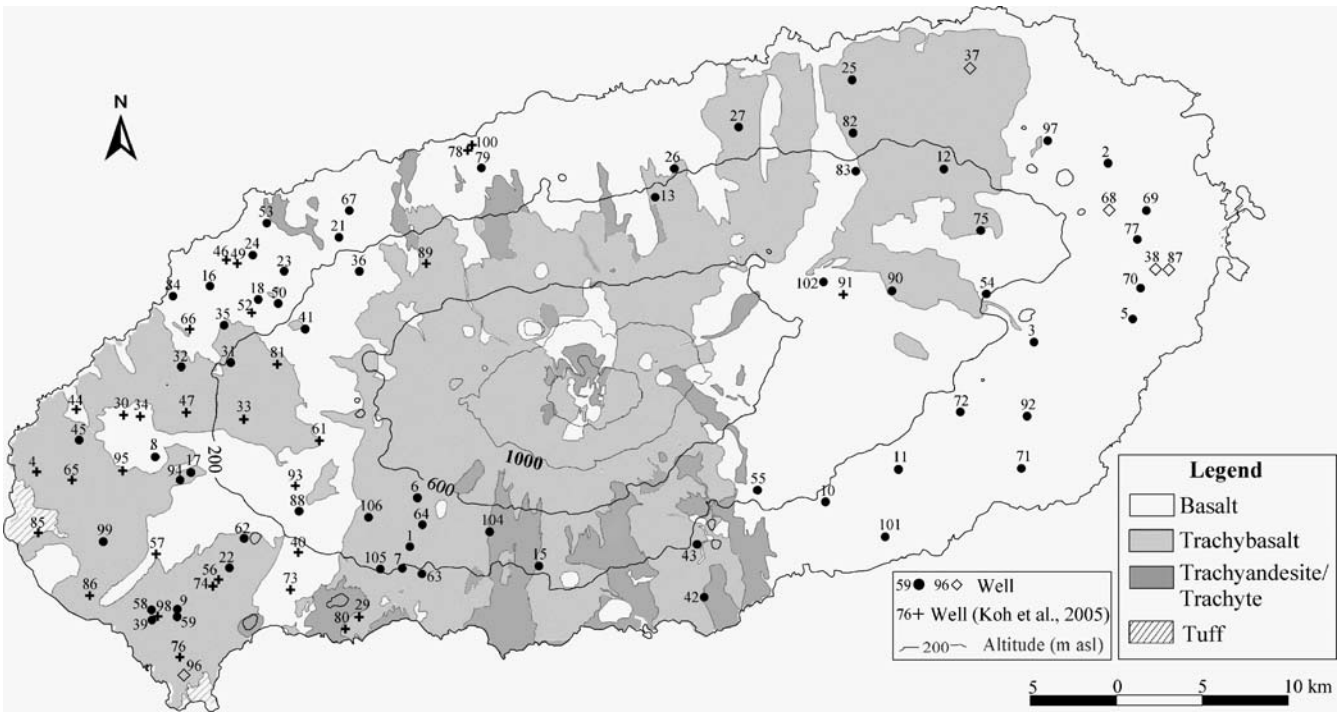

Fig. 6 Surficial geology map of Jeju Island with groundwater sampling locations (*solid circles*). *Diamonds* are the groundwater samples showing the effect of salinization by seawater. See text for details. *Crosses* are the sites of Koh et al. (2005) which were considered in this study. Altitudes on the *contour lines* are in meters above sea level

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groundwater and seawater considering the coastal setting of the study area (Berner and Berner 1987). Evaporation of irrigated water is unlikely to be a major source of salinity to groundwater because the basaltic rocks, which constitute most of the surficial lithology, have a thin soil cover and high permeability (Jejudo 1997). The presence of Cl is not likely from interactions between groundwater and the basaltic rocks because the island has neither active volcanic activity nor significant geothermal characteristics (Join et al. 1997). Thus, it is assumed that the Cl remaining after correcting for the rainwater contribution originates from seawater and sea-salt aerosols. Other ions maintain a composition similar to seawater because major ions do not undergo appreciable change during the formation of sea salt (Berner and Berner 1987).

Agricultural sources of nitrate contamination have also been associated with increased Cl in groundwater (Hill 1982; Pionke and Urban 1985; Pawar and Shaikh 1995). When Cl and NO_3 concentrations are compared, Cl shows an increase that corresponds with an increase in nitrate concentrations (Fig. 4). The ratio of Cl/NO_3 was determined as 0.59 in meq/L (0.32 in mg/L) for nitrate-contaminated water with correction for rainwater contribution. The Cl above this ratio was assumed to originate from seawater and sea-salt deposition. Thus, the seawater Cl contribution can be subtracted from the measured Cl concentration of groundwater and given as

$$C_i'' = C_i' - S_i \cdot C_{Cl}' \quad \text{for uncontaminated water} \tag{3}$$

$$C_i'' = C_i' - S_i \cdot \left(C_{Cl}' - R_{Cl/NO3} \cdot C_{NO3}'\right) \quad \text{for nitrate} - \text{contaminated water} \tag{4}$$

where

C_i'' concentration of ion i corrected for rainwater and seawater contributions
S_i ratio of ion i to Cl in average seawater
$R_{Cl/NO3}$ ratio of Cl/NO_3 determined for nitrate-contaminated water

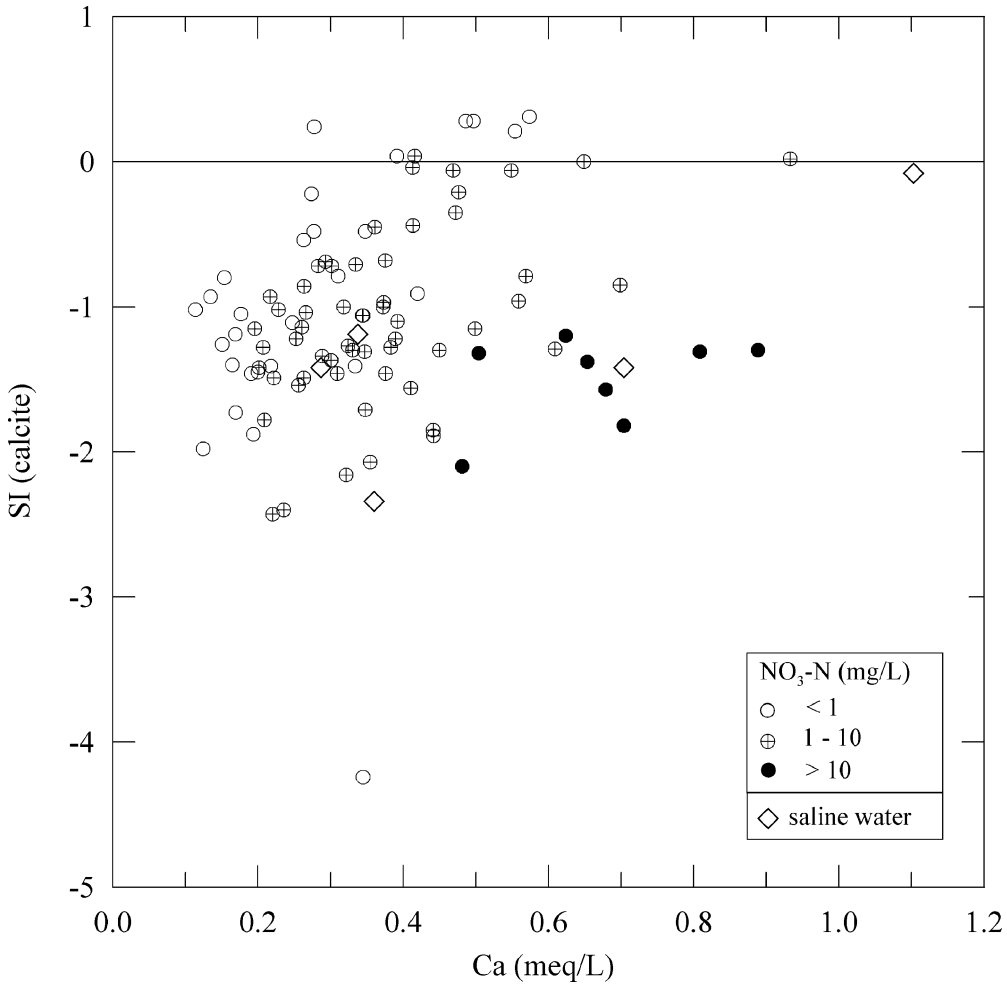

Fig. 7 Saturation indices (SI) of groundwater with respect to calcite

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Geochemical evolution of groundwater

The trends showing increasing cation and alkalinity concentrations are clearer when corrected for rainwater and seawater contributions (Fig. 5). Aquifer lithologies can be assigned as basaltic, trachytic rock and the sedimentary Seogwipo Formation at the wells utilized in this study (Fig. 6). However, the Seogwipo Formation was not considered here because (1) the formation is mainly located below surficial basaltic rocks and (2) its reactivity and chances for groundwater to encounter are limited compared to basaltic rocks, and (3) aquifer lithology frequently alternates between the Seogwipo Formation and basaltic rocks. Thus, the lithology at each well was determined as basaltic or trachytic considering surficial geology. The comparison between cations and alkalinity shows that cation concentrations associated with chemical weathering are not uniform (Fig. 5) and may undergo ion-exchange processes. Additionally, Na shows a higher release rate relative to alkalinity than other cations. This result indicates that Na released from chemical weathering, mainly due to the dissolution of basaltic glass, is not sensitive to the composition of basaltic rocks. Na also shows high mobility during weathering processes (Banfield et al. 1991). This high mobility suggests that Na trends can indicate weathering of basaltic rocks. There is no clear separation between the geochemistry of non-contaminated water quality for wells open to trachytic rocks compared to wells open to basaltic rocks (see also Fig. 6). Because basaltic rocks compose complex layers of lava flows and pyroclastic rocks with varying rock composition, surface lithology has little effect on the groundwater chemistry. However, samples collected from some wells open to trachytic rocks show lower ratios of Mg and Ca relative to alkalinity compared to samples from wells open to basaltic rocks. Groundwater is undersaturated with respect to calcite for most samples (Fig. 7), which was calculated in PHREEQC analysis (Parkhurst and Appelo 1999). This undersaturation indicates that Ca concentration is not affected by precipitation of carbonate minerals. Thus, lower Ca concentrations appear to be related to the smaller contents of mafic phenocrysts such as olivine and pyroxene, in trachytic rocks as compared to basalts.

Contribution of nitrate contamination

The effect of salinization and nitrate contamination on groundwater chemistry in the study area is also apparent when total cations and total alkalinity are compared (Fig. 8). With increased nitrate concentrations, groundwa-

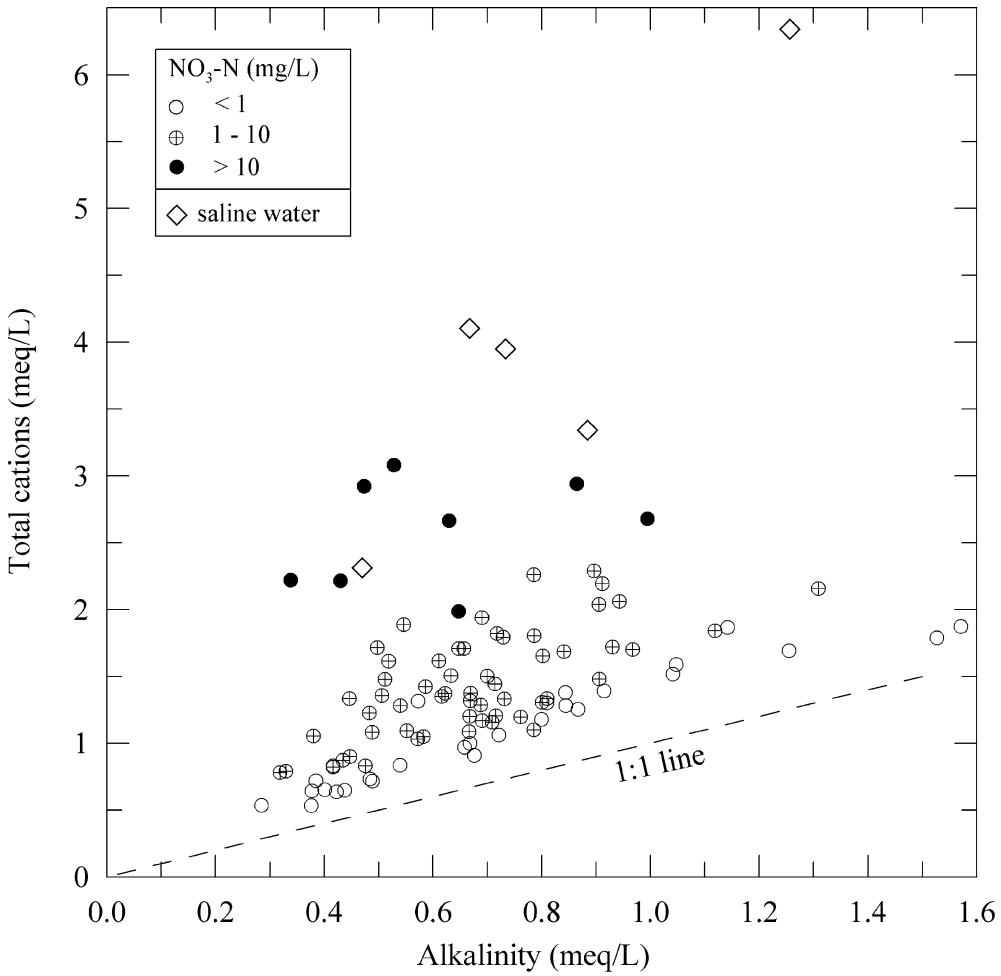

Fig. 8 Total cations vs. alkalinity in meq/L

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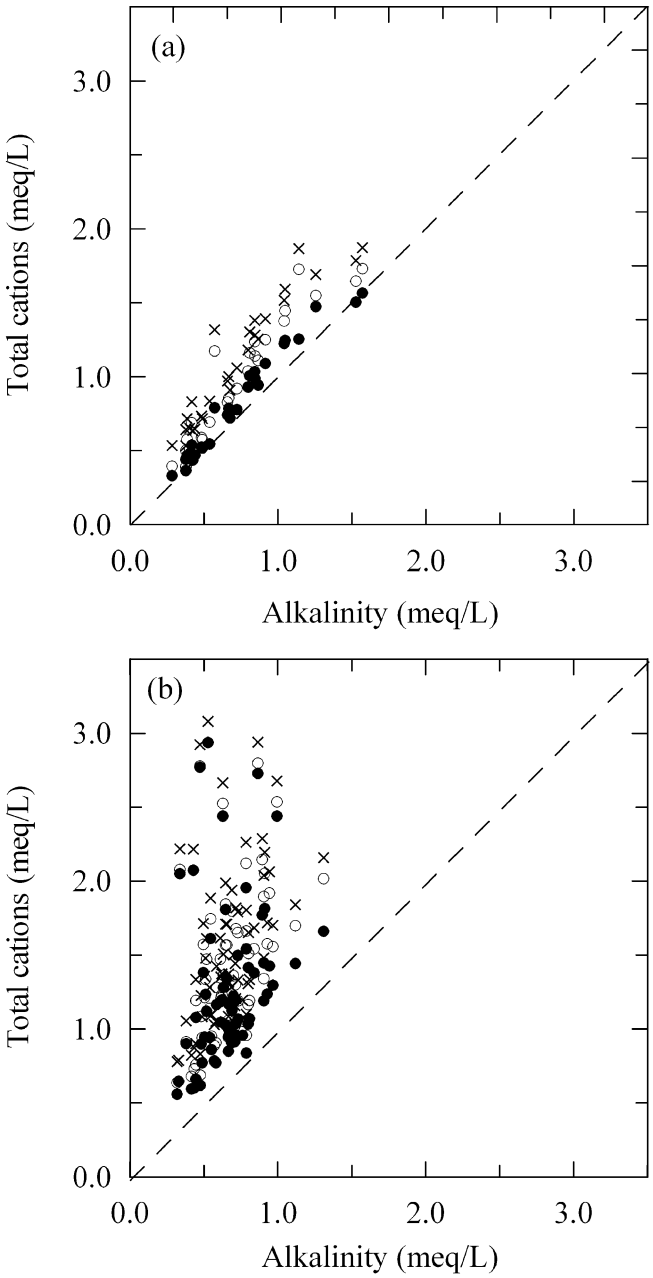

Fig. 9 Total cations vs. alkalinity with separation of geochemical processes. **a** Groundwater with nitrate concentration less than 1 mg/L NO_3–N, and (**b**) groundwater with nitrate concentration greater than 1 mg/L NO_3–N. *X* refers to measured concentrations, *open circles* are corrected concentrations for rainwater contribution, and *solid circles* are corrected concentrations for both rainwater and seawater contribution

ter chemistry deviates from non-contaminated water. Non-contaminated water chemistry is also away from the 1:1 line of total cations and total alkalinity. This result suggests that processes not associated with an increase in alkalinity contribute a large fraction of dissolved solutes. Where nitrate concentrations in groundwater are negligible, the samples approach the 1:1 line for total cations vs. alkalinity with correction for rainwater and seawater contributions (Fig. 9a). This result suggests that dissolved cations derived from chemical weathering were accompanied by an alkalinity increase for the non-contaminated groundwater. However, there is no such relation between total cations and alkalinity for groundwater when nitrate concentrations are greater than 1 mg/L NO_3–N, regardless of corrections for rainwater and seawater contributions. This result indicates that processes other than chemical weathering by CO_2 may contribute to the cation increase (Fig. 9b).

One source of cations in nitrate-contaminated groundwater is a simple dissolution of salts of Cl, NO_3, and SO_4 incorporated in the commercial fertilizers. In particular, Ca, and Mg are significantly incorporated in chemical fertilizers as nutrients for plants (Table 4). Thus, the excess cations after the absorption by growing plants can reach the water table and contribute solutes to groundwater.

It is also expected that chemical weathering promoted by the acidity generated as a result of N-fertilizer use can account for the considerable fraction of the increase in dissolved cations in nitrate-contaminated groundwater. If it is assumed that alkalinity is proportional to total cations released by chemical weathering by CO_2, which is the case for groundwater with negligible nitrate concentration, the increase in total cation concentrations from N-fertilizers, (T_{CAT}(NF), can be estimated by

$$T_{CAT}(NF) = T_{CAT}(M) - T_{CAT}(RW) - T_{CAT}(SW) - T_{CAT}(DF) - ALK, \quad (5)$$

where

T_{CAT}	equivalent concentration of total cations
NF	is contribution from N-fertilizers
M	is the measured concentration
RW	is the contribution from rainwater
SW	is the contribution from seawater
DF	is the contribution from the simple dissolution of fertilizers, which accompanied by Cl and SO_4
ALK	is the total alkalinity

Total cations from chemical fertilizers are above the 1:1 line with nitrate concentrations when including contributions both from N-fertilizer use, T_{CAT}(NF), and

Table 4 Chemical composition of complex chemical fertilizers used for major crops in Jeju Island (weight %)[a]

Crops	N	P	K	Ca	Mg	S	B
Mandarin oranges	10	14	10	9	3	4	0.3
Vegetables	12	8	12	6	3	4	0.3
Potatoes	11	9	13	5	3	3	0.3

[a] Data are taken from a report of one of the major manufacturers of chemical fertilizers in South Korea

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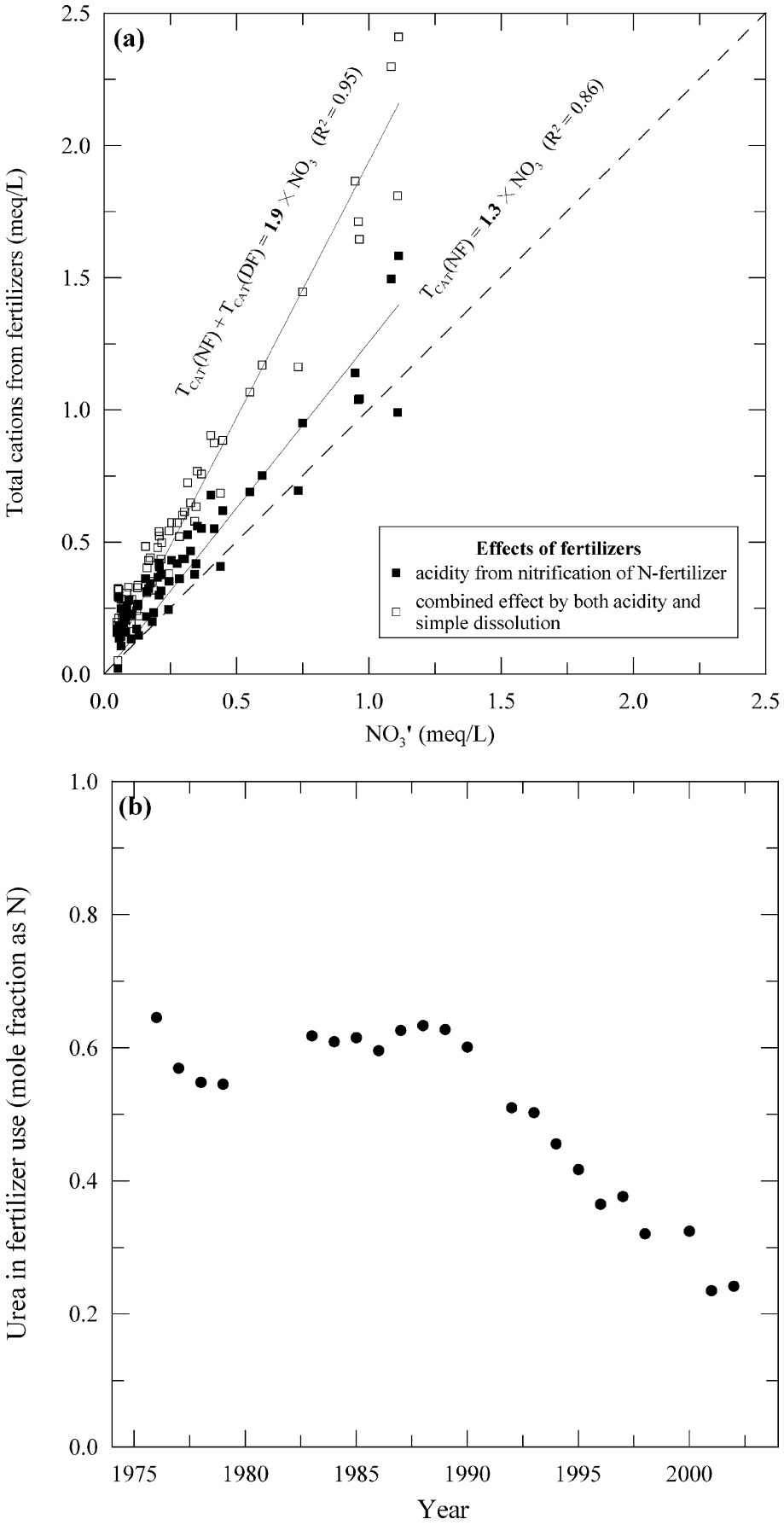

Fig. 10 **a** Total cations resulting from the use of chemical fertilizers for groundwater with nitrate concentrations greater than 1 mg/L NO_3–N. **b** Urea fraction of nitrogenous fertilizer use in Jeju Island. Data were obtained from the yearbooks of Jeju provincial government

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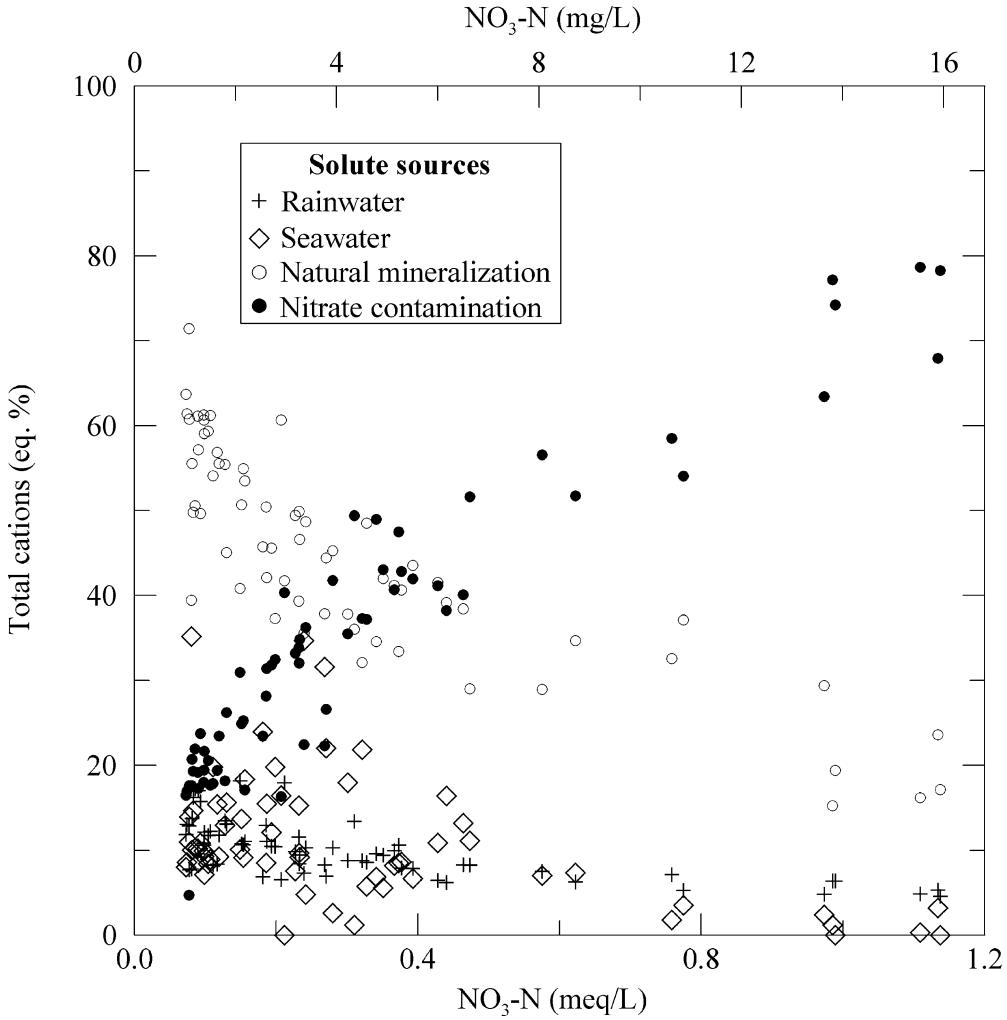

Fig. 11 Relative contribution of rainwater (*cross*), seawater (*diamond*), natural mineralization (*open circle*) that result in alkalinity increase, and nitrate contamination (*solid circle*) to total cations in groundwater

simple dissolution of fertilizers, T_{CAT}(DF), (Fig. 10a). However, after the contribution of simple dissolution was subtracted, total cations, that is T_{CAT}(NF), are still above the 1:1 line with nitrate concentrations. Nitrate in groundwater can be regarded as conservative because denitrification is unlikely given the relatively high dissolved-oxygen concentrations in groundwater underlying the study area (see Table 1). Thus, the increase in dissolved cation concentrations may be derived from chemical weathering promoted by acidity generated by N-fertilizers. In this context, the slope of T_{CAT}(NF) with respect to nitrate is the production coefficients of H^+ in the nitrification processes of nitrogenous compounds, which was shown in Eq. (1). The slope is similar to the production coefficients of H^+ in the nitrification of urea, which is a major nitrogenous compound in chemical fertilizers (Fig. 10b).

The proportions of total cations, Cl, and SO_4 in groundwater from various sources were estimated based on the sequential separation of the contribution of each geochemical process. Total cations derived from natural geochemical interactions between aquifer materials and groundwater have increased proportions when nitrate concentrations are low (Fig. 11). However, nitrate contamination sources (i.e., nitrate concentrations greater than about 6 mg/L NO_3–N) contribute the highest cation concentrations in groundwater. The average contribution of each geochemical process to total cations is 11, 11, 53, and 24% for rainwater, seawater and sea-salt deposition, natural mineralization, and nitrate contamination, respectively, excluding five samples with relatively high salinities. These average contributions are indicative of a significant influence of nitrate sources to the major element chemistry of groundwater. Actually, 18% of groundwater samples in this study have contamination-dominated chemistry where contribution of human inputs to total cations is largest.

A significant portion of the anions in groundwater are derived from nitrate sources. Cl in water samples in the study-area wells originates more from nitrate sources than from seawater, particularly when nitrate concentrations are greater than about 7 mg/L NO_3–N (Fig. 12). Rainwater also contributes SO_4 to groundwater. Nitrate sources, where nitrate concentrations are greater than about 7 mg/L NO_3–N, contribute much more SO_4 to groundwater than rainwater (Fig. 12).

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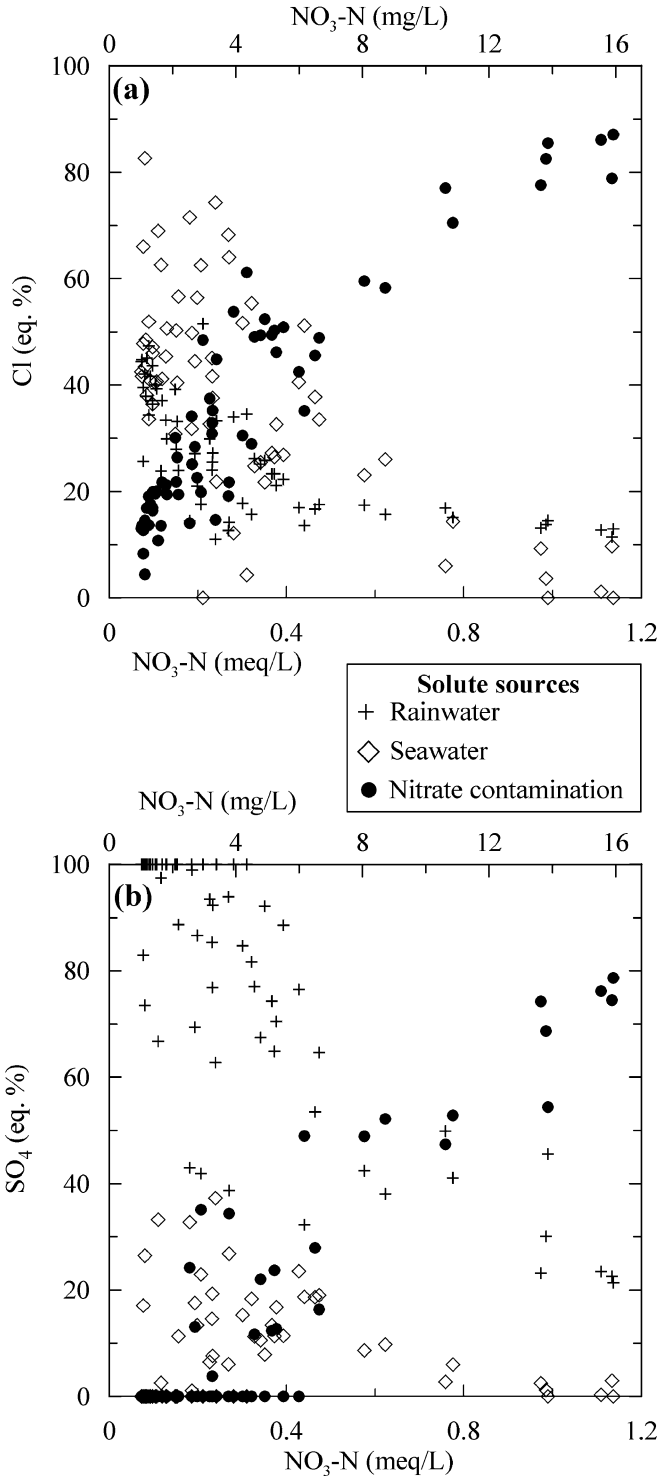

Fig. 12 Relative contribution of rainwater (*cross*), seawater (*diamond*), and nitrate contamination (*solid circle*) to Cl and SO_4 in groundwater

Analysis of the relative contribution of the four geochemical processes evaluated during this study shows that mineralization and dissolution processes resulting from soil acidity generated during nitrification of nitrogenous fertilizers predominate over other processes contributing to increased cation and nitrate concentrations.

Conclusion

Seawater and nitrate sources significantly affect the chemistry of groundwater in basaltic aquifers of Jeju Island, South Korea. This conclusion was shown by bivariate comparisons of major chemical constituents. Through factor analysis of the hydrogeochemical data, four geochemical processes, including rainfall recharge, seawater salinization and sea-salt deposition, nitrate contamination, and natural mineralization were identified. These processes were separated using a mass-balance approach that emphasized Cl as an indicator species. Nitrate-contaminated water correlates positively with cations, SO_4, and Cl. This correlation indicates that acidity generated during nitrification of nitrogenous fertilizers is considered a major source of nitrate in groundwater and also affects the overall groundwater chemistry.

Where groundwater is not affected by nitrate contamination, Na shows a higher correlation with HCO_3 than other cations with correction for rainwater and seawater contributions. Although the cation compositions in groundwater from basaltic and trachytic rocks are not distinguished, much lower Mg/HCO_3 and Ca/HCO_3 concentrations are observed in some groundwater flowing in trachytic rocks. Groundwater samples from the study area are generally undersaturated with respect to calcite. After correcting for rainwater and seawater contributions, total cations have a 1:1 relation with alkalinity in equivalent basis for non-contaminated water, whereas no correlation between total cations and alkalinity is observed for nitrate-contaminated water.

The total cations derived from nitrogenous fertilizers are higher than nitrate on an equivalent basis with a slope of 1.3. These results are similar to the production coefficients of H^+ in the nitrification of urea that is a major nitrogenous compound in chemical fertilizers. This is indicative of the possibility of chemical weathering promoted by acidity generated during nitrification of nitrogenous fertilizers. The contributions of major cations, Cl, and SO_4 to groundwater from nitrate sources, mainly chemical fertilizers, exceed contributions from other sources, particularly when nitrate concentrations are greater than 6–7 mg/L NO_3–N. On average, 24% of total cations in groundwater are estimated to derive from nitrate contamination sources in an equivalent basis and 18% of groundwater samples have a chemistry dominated by nitrate contamination.

Based on the statistical and mass-balance analyses of major element chemistry of groundwater, the hydrogeochemistry of basaltic aquifers in agricultural land usage underlying Jeju Island was significantly affected by nitrate and acidity during nitrification, and direct input from chemical fertilizers. Thus, regulation of agricultural land uses is necessary for the area where a major aquifer, especially utilized for drinking water, is located. Farming in the high-altitude area also needs to be assessed to determine the effects on groundwater quality because recharge in this area can significantly affect the coastal area where most people reside in Jeju Island.

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References

Adams S, Titus R, Pietersen K, Tredoux G, Harris C (2001) Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa. J Hydrol 241:91–103

Appelo CAJ, Postma D (1994) Geochemistry, groundwater and pollution. Balkema, Rotterdam, 536 pp

Banfield JF, Jones BF, Veblen DR (1991) An AEM-TEM study of weathering and diagenesis, Abert Lake, Oregon. I. Weathering reactions in the volcanics. Geochim Cosmochim Acta 55:2781–2793

Bang S-Y, Choi J-C, Park S-S, Cho K-S, Oh S-N (2003) A study on the properties of ionic components in precipitation at background area of the Korean Peninsula. J Korean Meteorol Soc 39:29–41

Bedient PB, Rifai HS, Newell CJ (1994) Groundwater contamination: transport and remediation. Prentice Hall, Englewood Cliffs, NJ, 541 pp

Berner EK, Berner RA (1987) The global water cycle: geochemistry and environment. Prentice-Hall, Englewood Cliffs, NJ, 397 pp

Bricker OP, Garrels RM (1967) Mineralogic factors in natural water equilibria. In: Faust SD, Hunter JV (eds) Principles and applications of water chemistry. Wiley, New York, pp 449–469

Cameron EM (1996) Hydrogeochemistry of the Fraser River, British Columbia: seasonal variation in major and minor components. J Hydrol 182:209–225

Collins R, Jenkins A (1996) The impact of agricultural land use on stream chemistry in the middle hills of the Himalayas, Nepal. J Hydrol 185:71–86

Davis JC (1986) Statistics and data analysis in geology. Wiley, New York, 646 pp

Eckhardt DAV, Stackelberg PE (1995) Relation of groundwater quality to land use on Long Island, New York. Ground Water 33:1019–1033

Ehrlich HL (1990) Geomicrobiology, 2nd edn. Dekker, New York, 646 pp

Evans CD, Davies TD, Wigington PJ Jr, Tranter M, Kretser WA (1996) Use of factor analysis to investigate processes controlling the chemical composition of four streams in the Adirondack Mountains, New York. J Hydrol 185:297–316

Garrels RM, Mackenzie FT (1967) Origin of the chemical compositions of some springs and lakes. In: Stumm W (ed) Equilibrium concepts in natural water systems. Am Chem Soc, pp 222–242

Grande JA, Gonzalez A, Beltran R, Sanchez-Rodas D (1996) Application of factor analysis to the study of contamination in the aquifer system of Ayamonte-Huelva (Spain). Ground Water 34:155–161

Hallberg GR, Keeney DR (1993) Nitrate. In: Alley WM (ed) Regional groundwater quality. Reinhold, New York, pp 297–322

Hill AR (1982) Nitrate distribution in the groundwater of the Alliston region of Ontario, Canada. Ground Water 20:696–701

Jejudo (1997) Report on the general investigation of the mountainous area in Jeju Island. Jeju Provincial Government, Jeju Island, 344 pp

Jejudo (2003) General investigation of hydrogeology and groundwater resources of Jeju Island (3). Jeju Provincial Government, Jeju Island

Jeong CH (2001) Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea. J Hydrol 253:194–210

Join J-L, Coudray J, Longworth K (1997) Using principal components analysis and Na/Cl ratios to trace groundwater circulation in a volcanic island: the example of Reunion. J Hydrol 190:1–18

Kang C-H, Kim W-H, Hong S-B, Lee K-H, Hong M-S, Shim S-G (1999) Analysis of rainwater in clean air area: characteristics of rainwater at 1100 site of Mt. Halla and Cheju City in 1997–1998 (in Korean). J KOSAE 15:555–566

Kim Y, Lee K-S, Koh D-C, Lee D-H, Lee S-G, Park W-B, Koh G-W, Woo N-C (2003) Hydrogeochemical and isotopic evidence of groundwater salinization in a coastal aquifer: a case study in Jeju volcanic island, Korea. J Hydrol 270:282–294

Koh D-C, Chang H-W, Lee K-S, Ko K-S, Kim Y, Park W-B (2005) Hydrogeochemistry and environmental isotopes of groundwater in Jeju volcanic island, Korea: implications for nitrate contamination. Hydrol Processes 19:2225–2245

Lee K-S, Wenner DB, Lee I-S (1999) Using H- and O-isotopic data for estimating the relative contributions of rainy and dry season precipitation to groundwater: example from Cheju Island, Korea. J Hydrol 222:65–74

McGahan DG, Southard RJ, Zasoski RJ (2003) Mineralogical comparison of agriculturally acidified and naturally acidic soils. Geoderma 114:355–368

Oh Y-K, Hyun I-H (1997) Estimation of nitrate-nitrogen contamination sources in Cheju Island groundwater using $\delta^{15}N$ values. J Korean Soc Groundwater Env 4:1–4

Oh J, Yi S, Yoon S, Koh G-W, Yun H, Lee J-D (2000) Subsurface stratigraphy of Jeju Island. J Geol Soc Korea 36:181–194

Pacheco FAL (1998) Application of correspondence analysis in the assessment of groundwater chemistry. Math Geol 30:129–161

Pacheco FAL, Szocs T (2006) "Dedolomitization reactions" driven by anthropogenic activity on loessy sediments, SW Hungary. Appl Geochem 21:614–631

Pacheco FAL, Van der Weijden CH (1996) Contributions of water–rock interactions to the composition of groundwater in areas with a sizeable anthropogenic input: a case study of the waters of the Fundao area, central Portugal. Water Resour Res 32:3553–3570

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2): a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. WRI 99-4259. US Geological Survey, Denver, CO, 312 pp

Pawar NJ, Shaikh IJ (1995) Nitrate pollution of groundwaters from shallow basaltic aquifers, Deccan Trap Hydrologic Province, India. Environ Geol 25:197–204

Pionke HB, Urban JB (1985) Effect of agricultural land use on groundwater quality in a small Pennsylvania watershed. Ground Water 23:68–80

Runnells DD (1993) Inorganic chemical processes and reactions. In: Alley WM (ed) Regional groundwater quality. Reinhold, New York, pp 131–154

Sharma ML, Hughes MW (1985) Groundwater recharge estimation using chloride, deuterium and oxygen-18 profiles in the deep coastal sands of Western Australia. J Hydrol 81:93–109

Sohn Y-K, Park J-B, Khim B-K, Park K-H, Koh G-W (2002) Stratigraphy, petrochemistry and Quaternary depositional record of the Songaksan tuff ring, Jeju Island, Korea. J Volcanol Geother Res 119:1–20

Song Y-C, Koh Y-K, U J-G (1999) Estimation of nitrate sources in Cheju Island groundwater using $\delta^{15}N$. J Korean Soc Groundwater Env 6:107–110

van den Brink C, Zaadnoordijk WJ (1995) Evaluation of groundwater contamination from nonpoint sources: a case study. Ground Water 33:356–365

Won C-K (1976) Study of petro-chemistry of volcanic rocks in Jeju Island. J Soc Geol Korea 12:207–226

Woo N-C, Kim H-D, Lee K-S, Park W-B, Koh G-W, Moon Y-S (2001) Interpretation of groundwater system and contamination by water-quality monitoring in the Daejung watershed, Jeju Island. Econ Environ Geol 34:485–498