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# Geostatistical techniques to evaluate groundwater contamination and its sources in Miryang City, Korea

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Abstract Miryang City has high seasonal variations in precipitation and small number of surface reservoirs. It uses much groundwater for living and irrigation purposes. This study delineates the characteristics and the controlling factors of groundwater contamination using multivariate statistical analyses and kriging method. GIS spatial maps showed that groundwater contamination was occurred mainly in the central and southern areas and partly in the southwestern and northern areas. It may be attributed to the effect of residual saline water, irrigation, livestock wastes and municipal sewage. Ca-HCO<sub>3</sub> water type was the most predominant in the groundwater of the study area. Ca-Cl<sub>2</sub>, Na-Cl and Na-HCO<sub>3</sub> water types were dominant in order, due to the influence of residual saline water and anthropogenic activity. Geostatistical techniques were applied to classify the groundwater samples and to identify the geochemical processes and sources controlling the groundwater geochemistry. The scatter diagrams of factor score versus topographic elevation and groundwater level represented that groundwater was influenced by saline water and NO3-N at <85 m of well elevation. The areas and degrees of groundwater contamination were understood from the

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spatial distribution maps of factor scores versus groundwater level. Chemical characteristics and contamination sources of groundwater were identified from cluster and factor analyses. Kriging method was useful for the production of distribution maps showing the degree and location of groundwater contamination. Thus, geostatistical techniques including factor analysis, cluster analysis and kriging method played very important roles in evaluating groundwater contamination and identifying contamination sources.

**Keywords** Geostatistical techniques · Groundwater contamination · Residual saline water · Factor analysis · Cluster analysis · Kriging

### Introduction

Groundwater has become the major source of water supply for domestic, agricultural and industrial demanders in the world. It is estimated that one-third of people in the world are using groundwater for drinking. Groundwater and surface water are the only sources of freshwater to encounter domestic, agricultural and industrial needs in coastal areas. Moreover, groundwater has been continuously threatened from the saline water, and it has drawn worldwide concerns (Amer 1995; Rajmohan et al. 1997; Melloul and Goldenberg 1998; Elampoornam et al. 1999; Ozler 2003; Terzic et al. 2008; Adepelumi et al. 2009). Groundwater quality is critically influenced by geological formations and anthropogenic activities. The studies of groundwater contamination can be helpful for taking appropriate measures of the aquifer protection from natural phenomena or anthropogenic activities. Generally, the municipal groundwater quality is affected by anthropogenic sources such as improperly treated industrial, municipal or domestic effluents. The influence of saline water is the major source of groundwater contamination in coastal cites (Chung et al. 2015; Venkatramanan et al. 2015a). Salinization of coastal aquifers is explained generally in terms of lateral seawater intrusion into the aquifer. However, other processes may be involved, such as flow of saline groundwater from adjacent or underlying aquifers, anthropogenic contamination due to agricultural return flow or infiltration of sewage and industrial effluents (Kass et al. 2005; Farber et al. 2007; Anithamary et al. 2012; Venkatramanan et al. 2012, 2013, 2015b). Seawater intrusion due to high evaporation and low and erratic rainfall in a coastal environment was reported by Rajmohan et al. (2007). Coastal aquifers are especially damaged by enhanced pumping for water supply, as this leads in some cases to water table lowering, increase in land subsidence and intrusion of saline water into freshwater aquifers (Andreasen and Fleck 1997; Capaccioni et al. 2005; Giambastiani et al. 2007; Trabelsi et al. 2007; Chidambaram et al. 2009).

Multivariate statistical analyses have been used for many applications to water quality assessment (Simeonov et al. 2003): identification of anthropogenic processes affecting groundwater chemistry of a semi-confined aquifer (Dragon 2006), the assessment of groundwater contamination sources (Singh et al. 2005) and the identification for the contamination source of marine water (Zhou et al. 2007). Kriging is especially useful for the synthetic analysis of groundwater quality or quantity data. The examples of kriging application are the following cases: the risk assessment of nitrate contamination (Hu et al. 2005), the evaluation of arsenic contamination potential (Liu et al. 2004), the analysis of surface water leakage into groundwater with geochemical analysis (Wang et al. 2001), and the optimization of groundwater level observation networks (Theodossiou and Latinopoulos 2006).

It is expected that this research can contribute to the identification of groundwater contamination sources and origins and to the effective protection and management of groundwater in Miryang City. This study used both multivariate analyses and kriging method. Also it evaluated the updated scientific basis of groundwater contamination and its sources in this region and may offer a valuable insight for future research.

# Study area settings

The Miryang City is located at the northeastern part of the Gyeongsang-do Province and is covered by  $798.98 \text{ km}^2$ . The longest distances between the east and the west and between the north and the south are 38 and 24.5 km, respectively. The city is surrounded by high mountains

excluding the southern part of a plain. The Nakdong River which is the longest in the South Korea meanders through the southern part of the city. The Miryang River flows through the center of the city and is merged to the Nakdong River (Fig. 1a). The geology of the study area has the Quaternary alluvium and the Cretaceous rocks which are the Jindong Formation of basal sedimentary rocks, the Yucheon Group of Chusan andesitic rocks and Unmunsa rhyolitic rocks, and the Bulguksa intrusive rocks of granites (Fig. 1c). The Bulguksa intrusive rocks form steep mountains at the eastern and the northern part of the study area. The Jindong Formation exists mainly at the eastern part and slightly at the western part. The Chusan andesitic rocks are distributed largely at the whole study area. The southern part of the study area forms the lowland of small hills and plains around the boundary of the Nakdong River.

Miryang City is located at the inland of the southern part, Korea, but groundwater in the city is influenced by the residual saline water because the Nakdong River is connected to the South Sea. However, seawater has not come to the city anymore because of a barrage in the front of the South Sea. The areas near the Nakdong River still have the influence of saline water. This city has two functions of an urban and rural area simultaneously. It is estimated that the contaminants of this city include sewage, saline water, salt pan deposits, fertilizer, pesticides, municipal and industrial wastes. Groundwater is relatively abundant to use for multi-purposes in this study area. Many people live in the area near the Nakdong River and the Miryang Stream. Groundwater level is <5 m below ground surface around the river area, and many groundwater wells are developed here. Rice farming is activated at this area. Field, rice paddy and vinyl greenhouse is developed at the valley area of mountains, and groundwater level in these area is ranged from 10 to 20 m below ground surface. In mountain areas, there are not many groundwater wells, and the groundwater level is ranged from 20 to 50 m below ground surface.

The average precipitation of the Miryang City is about 1246 mm/year during the recent 30 years (Annual Statistical Report of the Miryang City, 2011). This city has high rainfall variations, i.e., high precipitation from June to August and low precipitation during other periods (Fig. 2). There are 1876 wells in this city: 987 wells for domestic use, 848 wells for agricultural use and 41 wells for industrial use. Most of wells belong to the private property, even though small number of wells was developed by official purpose. The city uses much groundwater of  $17 \times 10^6$  m<sup>3</sup>/year including  $11 \times 10^6$  m<sup>3</sup>/year for domestic use,  $5 \times 10^6$  m<sup>3</sup>/ year for agricultural use and  $1 \times 10^6$  m<sup>3</sup>/year for industrial use. About 70 % of wells were developed in bedrocks and 30 % in alluvium and completely or highly weathered rocks, because the thickness of alluvium is shallow and <10 m in average. The depth of wells is normally <100 m, but some



Fig. 1 Location and geology of Miryang City. a Location map. b Sampling wells. c Geological map



Fig. 2 Annual rainfall precipitation of Miryang City in 2011

wells are over 300 m. Most of groundwater is produced from fractured rocks in the city. The groundwater level is usually 2.6 and 7 m below ground surface in alluvium and bedrock, respectively.

# Materials and methods

# Groundwater sampling and analysis

Groundwater samples were collected from 76 bore wells developed in bedrock and were relatively uniformly distributed in the study area (Fig. 1b). The depth of sampling

wells ranged from 50 to 210 m, and the period of the sampling was in November, 2011. The locations of the sampling wells were marked by using GPS (Garman 76CSx). The samples were filtered with 0.45-µ Millipore filters and analyzed for chemical constituents. Methods of collection and analysis for groundwater samples were essentially followed the guideline of American Public Health Association (APHA 1995). pH, electrical conductivity (EC) and total dissolved solid (TDS) were measured in the field by model of Therm Orion 250A<sup>+</sup> (USA) and TOA CM-14P (Japan). HCO<sub>3</sub> and CO<sub>3</sub> were measured with titration method of pH in the field. Major elements and trace elements were analyzed in the laboratory using atomic absorption spectrometer (AAS, PerkinElmer 400) and ion chromatography (IC, Water 431). NO<sub>3</sub>-N and F were analyzed by using ion-sensitive electrode. Standards and blanks were run regularly to check accuracy of the procedures. All chemicals used were of analytical grade and obtained from Merck. The accuracy of analytical experiments was determined by calculating the ionic balance error, which was generally within  $\pm 5$  %.

#### **Factor analysis**

To transform the variable data into an easily interpretable form, factor analysis was undertaken using a routine model expressed as

$$x_j = \sum_{r=1}^p a_{j,r} f_r + \varepsilon_j \tag{1}$$

where  $x_j$  is the *j*th observed variable,  $f_r$  is the *r*th common factor, *p* is the specified number of factors and  $\varepsilon_j$  is the random variation unique to the original variable  $x_j$ . The coefficient  $a_{j,r}$  is the loading of the *j*th variate on the *r*th factor. It corresponds to a loading or weight in principal components (Davis 2002).

#### Factor rotation

The varimax criterion needs maximization of the variance of the loading on the factor. The variance  $s_k^2$ , of the loading on the *k*th factor, is defined as

$$s_k^2 = \frac{p \sum_{j=1}^m \left(a_{jp}^2 / h_j^2\right)^2 - \left(\sum_{j=1}^m \left(a_{jp}^2 / h_j^2\right)^2\right)}{p^2}$$
(2)

where *p* is the number of factors, *m* is the number of original variables,  $a_{jp}$  is the loading of variable *j* on factor *p* and  $h_j^2$  is the communality of the *j*th variable. The quantity to maximize is

$$V = \sum_{k=1}^{p} s_k^2 \tag{3}$$

The variance is calculated from the factor loading,  $a_{jp}$ , which are corrected by dividing each by its communality,  $h_j^2$  (Davis 2002). The Kaiser–Meyer–Olkin (KMO) measure and the Bartlett test of sphericity were carried out to evaluate the suitability of groundwater quality data for factor analysis. The distribution of groundwater components was transformed to be a log-normal distribution for the factor analysis. Principal component analysis (PCA) was used for the factor extraction, and the eigenvalues larger than 1.0 were chosen as factors. To maximize the variance of the loadings on the factor, the varimax orthogonal rotation technique was used. If the absolute value of a factor loading was over 0.5, it was considered to be a very important variable.

#### **Cluster analysis**

Comparisons based on the multiple parameters from different samples were made and its grouped based on the similarity to each other. Sampling wells and chemical constituents grouping was known as Q-mode classification. In this present study, O-mode cluster analysis was used to classify the samples and constituents based on the Ward's linkage method (Ward 1963). It was applied to normalized data using squared Euclidean distances as a measure of similarity. It is an extremely powerful grouping mechanism and uses the analysis of variance approach to evaluate distances between clusters, attempting to minimize the sum of squares of any clusters that can be formed at each step. It needs the standardization of sample data, because each component of water quality has a different unit. Standardization of data ensures that each variable has the same influence in the analysis.

#### **Ordinary kriging**

Kriging is a local estimation technique which provides the best linear unbiased estimator (BLUE) of the unknown data. Kriging can be expressed as

$$Z_K^* = \sum_{i=1}^n \lambda_i Z_i \tag{4}$$

where  $Z_K^*$  is estimator by kriging,  $\lambda_i$  is weight that is apportioned to  $Z_i$  and  $Z_i$  is value of spatial variable. The weight by kriging is calculated to ensure that the estimator is unbiased and that the estimation variance is minimal (Journel and Huijbregts 1978).

The unbiased condition of kriging can be expressed as  $E[Z_V - Z_K^*] = 0$  (5)

where  $Z_V$  is a true value and  $Z_K^*$  is an estimated value. The sum of weights is

$$\sum_{i=1}^{n} \lambda_i = 1.0 \tag{6}$$

The estimation variance or kriging variance can be expressed as

$$\sigma_K^2 = E\left\{ \left[ Z_V - Z_K^* \right]^2 \right\} = \overline{C}(V, V) + \mu - \sum_{i=1}^n \lambda_i \overline{C}(v_i, V)$$
(7)

where  $\overline{C}(V, V)$  is covariance between spatial variables,  $\mu$  is Lagrange parameter and  $\overline{C}(v_i, V)$  is covariance between spatial variables and an estimate. In this study, ordinary kriging was selected as the interpolation method. Semivariogram was created to evaluate the spatial structure of data values. From this analysis of the experimental variogram, a suitable model was spherical. The interpretation of multivariate statistical analysis and ordinary kriging was carried out by the software packages of SPSS (Ver.17), SURFER (Ver.12) and Arc GIS (Ver.10.2).

#### Results

#### Groundwater chemistry

Table 1 shows the descriptive statistical analysis of chemical compositions in groundwater. pH, EC and TDS value of groundwater samples are varied from 6.14 to 9.0, 33.90-3480 (µS/cm) and 23.80-2440 (mg/L), respectively. The high concentrations of cations are Ca (292 mg/L), Na (403.2 mg/L), Mg (121.72 mg/L) and K (21.4 mg/L), while those of anions are Cl (862.61 mg/L), SO<sub>4</sub> (648.53 mg/L), HCO<sub>3</sub> (246.44 mg/L), CO<sub>3</sub> (5.28 mg/L) and F (4.85 mg/L). Sodium (41.42) has the highest standard deviation in cations, and chloride (99.68) has the highest standard deviation in anions. The mean concentrations of heavy metals are Sr (0.45 mg/L), Mn (0.29 mg/ L), Zn (0.10 mg/L), Li (0.03 mg/L), Ba (0.03 mg/L), As (0.02 mg/L) and Fe, Al, Pb, Cu, Ni, Co (0.01 mg/L). Most of groundwater has good quality for drinking, but some groundwater exceeds the Korean standard level of drinking

Table 1 General statistics of chemical components in groundwater (unit: mg/L)

Variable	Maximum	Minimum	Mean	Median	Standard dev.	Korean drinking standard (2011)	WHO (2004)
рН	9.0	6.14	7.0	6.83	0.62	5.8-8.5	6.5-8.5
EC (µS/cm)	3480	33.90	433.8	250.3	544.8	_	1400
TDS	2440	23.80	293.8	171.6	376.7	500	500-1500
Na	290	5.11	26.49	14.30	41.42	_	200
К	21.40	0.02	1.90	0.92	3.30	-	10
Ca	292	2.86	36.26	24.45	48.49	-	200
Mg	121.72	0.29	8.56	5.91	14.50	-	150
Cl	262.6	0.12	27.33	12.88	99.68	250	250-600
HCO <sub>3</sub>	246.44	8.54	73.76	68.32	51.01	-	300
$SO_4$	648.53	0.50	28.92	6.25	87.94	200	200-400
CO <sub>3</sub>	5.28	1.32	3.30	3.30	2.80	-	_
NO <sub>3</sub> -N	62.49	0.02	6.37	3.97	10.00	10	50
SiO <sub>2</sub>	23.90	5.91	14.91	15.20	4.25	-	_
Sr	5.02	0.01	0.45	0.20	0.85	-	_
F	4.85	0.01	0.19	0.06	0.59	1.5	1.5
Mn	2.96	0.01	0.29	0.04	0.56	0.3	0.4
Zn	1.72	0.01	0.10	0.05	0.22	3	3
Li	0.26	0.01	0.03	0.01	0.04	-	_
Ba	0.13	0.01	0.03	0.02	0.03	-	0.3
Fe	0.03	0.01	0.01	0.01	0.01	0.3	0.3
Al	0.02	0.01	0.01	0.01	0.00	0.2	0.2
Pb	0.02	0.01	0.01	0.01	0.00	0.01	0.01
Cu	0.01	0.01	0.01	0.01	0.00	1	0.5
Ni	0.01	0.01	0.01	0.01	0.00	_	0.02
Co	0.01	0.01	0.01	0.01	0.00	_	_
As	0.09	0.01	0.02	0.01	0.02	0.01	0.01



Fig. 3 Spatial distribution maps for the concentrations of major cations and anions in groundwater

(2011) and WHO (2004) in the components of Cl, SO<sub>4</sub>, NO<sub>3</sub>-N, As, Zn and Mn.

#### **GIS** maps

Spatial distribution maps (Fig. 3) for the concentration of major components were produced by kriging interpolation method of ArcGIS (Ver. 10.2). In Na and Cl maps, the high concentration positions are located at the same areas, i.e., the central and southern parts. In Ca and SO<sub>4</sub> maps, the high concentration positions are located at the same areas, i.e., the central and northern parts. In Ca and HCO<sub>3</sub> maps, the high concentration positions are located at similar areas, i.e., the central and southwestern parts except the northern and southern parts. In K and Mg maps, the high concentration positions are located at the same areas, i.e., southern parts. In NO<sub>3</sub>-N and HCO<sub>3</sub> maps, the high concentration positions are located at similar areas, i.e., the central and southwestern parts except the southern parts. In NO<sub>3</sub>-N and HCO<sub>3</sub> maps, the high concentration positions are located at similar areas, i.e., the central and southwestern parts except the southern parts.

Groundwater types were classified according to the Piper plot (Piper 1953). By the spatial maps of groundwater types (Fig. 4), Ca-(HCO<sub>3</sub>) is the most dominant type, and Na-HCO<sub>3</sub>, Ca-Cl<sub>2</sub> and Na-Cl types are dominant in order. Ca-(HCO<sub>3</sub>) type is distributed throughout the study area, while Na-HCO<sub>3</sub> type is shown as the small patches in the whole study area. Ca-Cl<sub>2</sub> and Na-Cl types exhibit at the central and southern parts.

#### Statistical interpretation

Table 2 shows that the cations of Na, K, Ca and Mg have significant correlations over 0.76 each other. In anions, Cl has a little correlation of 0.57 only with Ca, while  $HCO_3$  has good correlations over 0.63 with Na, Ca and Mg.

The KMO measure is 0.744, and the Bartlett test of sphericity shows that the correlation matrix doesn't form a unit matrix. Thus, groundwater samples are suitable for the factor analysis. Based on the factor analysis (Table 3),



Fig. 3 continued

chemical components of Na, K, Ca, Mg, Cl, HCO<sub>3</sub> and SO<sub>4</sub> belong to factor 1, and NO<sub>3</sub>-N belongs to factor 2. The percentages of variance produced by factor 1 and factor 2 are 56.2 and 14.3 %, respectively, and 70.5 % in total. Na, Ca, Mg, Cl, HCO<sub>3</sub> and SO<sub>4</sub> of high factor loadings in factor 1 are abundant components in seawater as well as in fresh groundwater. NO<sub>3</sub>-N of factor 2 is related to agricultural fertilizer, livestock wastes and municipal sewage.

The scatter diagrams (Fig. 5) show the relation with factor scores for each of two factors versus topographic elevations and groundwater levels of monitoring wells. Four graphs show similar patterns of the relation with two factor scores versus topographic elevations and groundwater levels. The factor scores 1 and 2 of groundwater wells <85 m in topographic elevation range from -1.2 to 3.4 and -2.6 to 1.9, respectively (Fig. 5a, b). The factor scores 1 and 2 of groundwater level range from -1.2 to 3.4 and -2.6 to 1.9, respectively (Fig. 5c, d). The factor scores 1 and 2 of groundwater wells <80 m in groundwater level range from -1.2 to 3.4 and -2.6 to 1.9, respectively (Fig. 5c, d). The factor scores 1 and 2 of groundwater wells

over 85 m in topographic elevation or over 80 m in groundwater level have the negative values.

Cluster analysis was carried out to make groups of groundwater monitoring wells with chemical constituents. It plays an important role in interpreting the data and indicating patterns. Dendrogram (Fig. 6) represents two groups of clusters for monitoring wells. Group 1 includes 52 monitoring wells, and group 2 contains 24 monitoring wells.

# Spatial maps of groundwater levels with factor scores

Ordinary kriging was used to produce the distribution maps of 324 groundwater levels over the mean sea level. The spatial maps were used to understand correlations between factor scores of two factors and groundwater level. Variogram model was suitable for the nested types of spherical model (Kim et al. 2012; Venkatramanan et al. 2015a).

Fig. 4 Spatial distribution map of groundwater types



Table 2	Correlation matrix
between	groundwater quality
variables	

Variable	Na	K	Ca	Mg	Cl	HCO <sub>3</sub>	$SO_4$	NO <sub>3</sub> -N
Na	1.00							
K	0.94	1.00						
Ca	0.88	0.76	1.00					
Mg	0.96	0.92	0.88	1.00				
Cl	0.38	0.29	0.57	0.34	1.00			
HCO	0.63	0.51	0.74	0.65	0.40	1.00		
$SO_4$	0.24	0.08	0.43	0.10	0.58	0.16	1.00	
NO <sub>3</sub> -N	-0.05	-0.06	0.18	0.01	0.48	0.13	0.06	1.00

Significant values are in bold

Factor scores of F1 and F2 are indicated on the maps of groundwater level (Fig. 7a, b). Larger red circle is more significant for two factors, while larger blue circle is less significant for two factors. Higher groundwater levels are noted in the patches of eastern and northeastern parts.

# Discussion

pH level in groundwater indicates a low acidic due to the dissolved atmospheric carbon dioxide and CO<sub>2</sub> in soils. High EC and TDS may be attributed to the influence of saline water or contaminants. Na concentration of groundwater samples designates the influence of saline water or salt pan deposits. Moreover, Na and Ca are derived from the dissolution of plagioclase minerals. The major source minerals of Mg are biotite and chlorite minerals. K component indicates the weathering of feldspar or the presence of clay minerals in the aquifer matrix. HCO<sub>3</sub> and CO<sub>3</sub> are derived from the source of CO<sub>2</sub> action upon the basic materials of soil and lithology. F concentration in groundwater indicates the dissolution of granitic rocks and anion exchange with micaceous minerals. Cl is derived from saline water influence, or other non-lithological source. Natural Cl ion concentration arises from three major sources, viz. solution of halite (NaCl) and related

Table 3 Factor analysis for groundwater quality variables

Variable	Factor 1	Factor 2	Communality
Log Na	0.92	-0.13	0.87
Log K	0.58	-0.17	0.36
Log Ca	0.93	0.04	0.87
Log Mg	0.86	-0.08	0.74
Log Cl	0.83	0.40	0.85
Log HCO <sub>3</sub>	0.79	-0.12	0.66
Log SO <sub>4</sub>	0.61	0.26	0.44
Log NO <sub>3</sub> -N	-0.06	0.93	0.86
Eigen value	4.49	1.15	
% of variance	56.2	14.3	

Significant values are in bold

minerals in evaporate deposits, ancient seawater entrapped in sediments and atmosphere deposit (Walker et al. 1991). Anthropogenic sources of Cl in groundwater may also be due to the influences of irrigation return flows and chemical fertilizers (Marie and Vengosh 2001; Subba Rao et al. 2012). Higher concentration of chloride in the coastal region may be due to seawater intrusion (Jalali 2007; Chidambaram et al. 2010; Ramkumar et al. 2011; Subba Rao et al. 2012; Venkatramanan et al. 2015a), whereas  $SO_4$ concentration in groundwater may be due to the action of leaching and anthropogenic activities in a geochemical environment by release of sulfur gases from industries, and urban utilities oxidized and inflowed into the groundwater system (Saxena et al. 2004). Salt pans/seawater intrusion can be responsible for most of  $SO_4$  inputs into the



Fig. 5 Plots of factor scores versus elevation and groundwater levels.  $\mathbf{a}$  F1 versus elevation.  $\mathbf{b}$  F2 versus elevation.  $\mathbf{c}$  F1 versus groundwater level.  $\mathbf{d}$  F2 versus groundwater level



Fig. 6 Dendrogram of the Q-mode cluster analysis

groundwater samples (Barbecot et al. 2000). The highest  $SO_4$  content of the groundwater samples indicates the influence of marine source due to gypsum (CaSO<sub>4</sub>·H<sub>2</sub>O), as amendment to alter the physical and/or chemical properties of the soils. This may be expected to be caused by the higher concentration of SO<sub>4</sub> in the study area, as there are no probable lithological sources (Subba Rao et al. 2012). The higher concentration of NO<sub>3</sub>-N is an indication of anthropogenic pollution. It indicates the influences of agricultural and domestic effluents (Subba Rao et al. 2012). Heavy metal concentrations of the present study exist within the permissible limit, except As and Mn. The heavy metals may be due to the influence of agriculture and industrial effluents and also lithogenic origin.

GIS spatial maps of Na, K and Ca, it is thought that most of the components were derived from the direct cation exchange process through saline water and lithogenic origin. HCO<sub>3</sub> may be attributed to the dissolution of CO<sub>2</sub> gas in the air or soil into water, and the irrigation return flow containing carbonate minerals precipitated in the soil, while Mg was derived from agriculture and domestic wastes. Cl might come from residual saline water, irrigation return flow and many kinds of contaminants. SO<sub>4</sub> was influenced by saline water, irrigation effluents and dissolution of sulfide minerals. NO<sub>3</sub>-N came from the pollution sources like fertilizers, sanitation facilities and domestic effluents. Based on the groundwater types, Ca-HCO<sub>3</sub> and Na-HCO<sub>3</sub> were the dominant water type because of various natural reactions and anthropogenic contaminations. Ca-Cl and Na-Cl type were polluted by saline water and other anthropogenic inputs (Jeong 2001).

The correlation matrix shows that there is a good relationship between the chemical constituents. Influence of seawater intrusion and irrigation waste effluents increases the ionic concentration in groundwater. It is observed that HCO<sub>3</sub> with Na indicates mineral dissolution. Factor analysis exhibits that factor 1 is influenced by seawater. The Nakdong River is located at the southern boundary of the Miryang City and is flowing to the eastern side. It is intruded by the seawater of the South Sea in Korea. The high concentration of SO<sub>4</sub> is related to mixing with seawater. The association of Ca and K due to the leaching of secondary salts (Panagopoulos et al. 2004; Prasanna et al. 2009), and F,  $CO_3$  and  $HCO_3$  indicates the chemical weathering of minerals. NO<sub>3</sub>-N of factor 2 is the main component of groundwater contamination in Korea. NO3-N is an important indicator of anthropogenic influence, i.e., fertilizer, sewage and livestock wastes.

Scatter diagrams of factor scores versus topographic elevation (Fig. 5a, b) support that the influence of saline water and NO<sub>3</sub>-N contamination is more popular at the <85 m of topographic elevation than higher areas. Scatter diagrams of factor scores versus groundwater level (Fig. 5c, d) represent that groundwater contamination is more popular at the <80 m of groundwater level than higher level areas. It is because low-level areas are more



Fig. 7 Maps showing the relation between factor scores and groundwater level. a F1 versus groundwater level. b F2 versus groundwater level

vulnerable against groundwater contamination than higher areas. Dendrogram of Q-mode cluster analysis (Fig. 6) reveals that group 1 and group 2 belong to Ca-HCO<sub>3</sub> type of freshwater and Na-HCO<sub>3</sub> type slightly affected by seawater, respectively. Group 3 covers Na-Cl and Ca-Cl types heavily influenced by seawater.

In F1 factor score versus groundwater level (Fig. 7a), red circles indicate the groundwater contaminated by saline water or anthropogenic sources, and blue circles represent the freshwater. Larger red and larger blue circles indicate more contaminated and fresher groundwater, respectively. The groundwater of the south and the southwest parts is more contaminated, and groundwater of other areas is mostly fresh. In F2 factor score versus groundwater level (Fig. 7b), red circles indicate the groundwater contaminated by NO<sub>3</sub>-N, and blue circles represent uncontaminated groundwater. NO<sub>3</sub>-N contamination is more widely distributed than F1 contamination, because it is related mainly to agricultural fertilizer, municipal sewage and livestock wastes. Groundwater in the southern part is free from NO<sub>3</sub>-N N contamination. The mountain areas of higher groundwater level in the eastern and the western parts exhibit the contamination of NO<sub>3</sub>-N.

# Conclusions

We conclude the following important aspects from this study:

- Most of groundwater has good quality for drinking, but some groundwater exceeds Korea and WHO standard levels of drinking in the components of Cl, SO<sub>4</sub>, NO<sub>3</sub>-N, As, Mn and F. Ca-HCO<sub>3</sub> type is the most predominant in this area, and Ca-Cl, Na-Cl and Na-HCO<sub>3</sub> types are in order. Ca-Cl, Na-Cl and Na-HCO<sub>3</sub> types suggest the effects of residual saline water and anthropogenic activity in the study area.
- The correlation matrix shows that the cations of Na, K, 2. Ca and Mg have significant correlations over 0.76 each other. In anions, Cl has a little correlation of 0.57 only with Ca, while HCO<sub>3</sub> has good correlations over 0.63 with Na, Ca and Mg. Based on the factor analysis, Na, K, Ca, Mg, Cl, HCO<sub>3</sub> and SO<sub>4</sub> belong to factor 1, and NO<sub>3</sub>-N belongs to factor 2. Factor 1 is related to the seawater effect, and factor 2 is related to the nonpoint sources of agricultural fertilizer, livestock wastes and municipal sewage. Scatter diagrams of factor scores versus topographic elevation and groundwater level support that the influence of saline water and NO<sub>3</sub>-N contamination is more popular at the <85 m of topographic elevation and at the <80 m of groundwater level, respectively.
- 3. By cluster analysis, groundwater is classified into three groups, i.e., Ca-HCO<sub>3</sub> type of freshwater, Na-HCO<sub>3</sub> type slightly affected by seawater, and Na-Cl and Ca-Cl types heavily influenced by seawater. F1 factor score versus groundwater level indicates that the groundwater of the southern and the southwestern parts is more contaminated by saline water, and groundwater of other areas is mostly fresh. F2 factor score versus groundwater level represents that NO<sub>3</sub>-N contamination is more widely distributed than F1 contamination, because it is related to the nonpoint

sources of agricultural fertilizer, municipal sewage and livestock wastes.

The vulnerability of groundwater contamination was 4. assessed from the scatter diagrams of factor scores versus topographic elevation and groundwater level. The areas and degrees of groundwater contamination were understood from the spatial distribution maps of factor scores versus groundwater level. Chemical characteristics and contamination sources of groundwater were found from cluster and factor analyses. Kriging method was useful for the production of distribution maps with some purposes showing the degree and location of groundwater contamination. Thus, geostatistical techniques including factor analysis, cluster analysis and kriging method played very important roles in evaluating groundwater contamination and identifying contamination sources.

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