Applied Geochemistry 45 (2014) 82–93

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Role of an impermeable layer in controlling groundwater chemistry in a basaltic aquifer beneath an agricultural field, Jeju Island, South Korea

Hee-Won Jung [a], Seong-Taek Yun [a,*], Kyoung-Ho Kim [a], Sang-Sil Oh [b], Kyung-Goo Kang [c]

[a] Department of Earth and Environmental Sciences and KU-KIST Green School, Korea University, Seoul 136-701, South Korea
[b] Jeju Special Self-Governing Province Institute of Environment Research, Jeju, South Korea
[c] Jeju Special Self-Governing Province Development Corporation, Jeju, South Korea

ARTICLE INFO

Article history:
Available online 22 March 2014
Editorial handling by M. Kersten

ABSTRACT

Hydrochemical data (major cations and anions, and trace metals such as Fe, Mn and V) of groundwater ($n = 144$) were collected from 15 pre-existing wells in the Gosan area, along the southwestern coast of Jeju Island, South Korea, between January and October 2010. These were used to investigate the spatio-temporal variability of groundwater quality in a basaltic aquifer beneath an agricultural field. In the western part of the study area, an impermeable clay-rich layer (Gosan Formation) overlies the basaltic aquifer, prohibiting direct recharge from rainwater infiltration and allowing a shallow perched aquifer to form above the formation. Robust Principal Component Analysis (ROBPCA) was performed to investigate the hydrochemical characteristics. Twenty-seven outlying samples were separated from the total dataset; among these, 17 samples reflected seawater effects, and seven samples reflected abnormally high impacts from agricultural contamination. For the rest regular observations ($n = 117$) and a good leverage point, ROBPCA showed that principal component (PC) 1 effectively distinguishes uncontaminated water from those samples reflecting agricultural contamination. Variables with positive PC 1 loadings (TDS, Ca, Mg, NO_3, SO_4, and Cl) indicate agricultural contamination, while negative PC 1 loadings (pH, Na, K, HCO_3 and V) possibly indicate basalt weathering. Samples with chemistry controlled by agricultural contamination are restricted to the eastern part of the study area, while uncontaminated water is predominantly observed in the western part where the Gosan Formation occurs. Such a distinct spatial pattern indicates that overall groundwater quality is regulated by the occurrence of the impermeable formation. Groundwater samples from wells near the edge of the Gosan Formation show seasonal fluctuations in water quality, with factor scores that indicates uncontaminated water in the dry season (January to April), and agricultural contamination in the wet season (May to October). This suggests that groundwater below the marginal part of the impermeable layer is seasonally contaminated by a temporal extension of the pollution front during the wet season, even though the impermeable layer plays a role as a natural barrier to protect groundwater from the infiltration of surface contaminants. This study also shows the advantage of ROBPCA to successfully identify spatio-temporal variation of groundwater quality in an area where diverse hydrochemical processes are coexisting and anormalous samples occur.

1. Introduction

Groundwater pollution arising from anthropogenic activities has become a significant global environmental issue. Among the various sources of anthropogenic contamination, agricultural activity is the most important, resulting in enrichments of solutes such as nitrate (Mengis et al., 2001; Böhlke, 2002; Nolan et al., 2002; Ritter et al., 2002; Gardner and Vogel, 2005; Chae et al., 2009; Chen et al., 2010). The vulnerability of groundwater to contamination is highly dependent on the geological characteristics of an area. For example, regions where surface contaminants can be rapidly transported into an aquifer are particularly susceptible to contamination (Nolan et al., 2002; Davraz et al., 2009; Jiang et al., 2009), while the presence of an impermeable layer may provide natural protection against contamination (Ebraheem et al., 1997; Conboy and Goss, 2000; Nishikiori et al., 2012). Therefore, it is crucial to evaluate groundwater quality in relation to geological features.

Groundwater on Jeju Island, South Korea, is known to be highly vulnerable to anthropogenic contamination because of the highly permeable nature of its volcanic rocks (Oh and Hyun, 1997;

* Corresponding author. Tel.: +82 2 3290 3176; fax: +82 2 3290 3189.
E-mail address: styun@korea.ac.kr (S.-T. Yun).

http://dx.doi.org/10.1016/j.apgeochem.2014.03.008
0883-2927/

Kim et al., 2007; Koh et al., 2005; Koh et al., 2007). Especially in the western part of Jeju Island, significant contamination of groundwater by nitrate from chemical fertilizers has been reported (Choung et al., 2004; Koh et al., 2005; Koh et al., 2006). The Gosan area has been an important coastal agricultural region since the 1970s, and is comprised of permeable basaltic rocks which are locally underlain by an impermeable clay layer (Park et al., 2000; Oh et al., 2009; Koh et al., 2012b). However, the role of this impermeable layer as a natural barrier to anthropogenic contamination and the spatio-temporal characteristics of the groundwater quality in the Gosan area have not yet been sufficiently investigated.

To identify the spatio-temporal patterns in water quality in an area, it is necessary to distinguish between groundwater contamination resulting from anthropogenic versus natural processes (i.e., water–rock interaction). This distinction is crucial for the sustainable management of groundwater and can be achieved by application of multivariate statistics. For such purposes, classical principal component analysis (CPCA) has been extensively used (Aiuppa et al., 2003; Locsey and Cox, 2003; Chae et al., 2006; Jiang et al., 2009; Choi et al., 2012). However, this method is very sensitive to anomalous observations; because the first components are attracted toward outlying points, the CPCA result with outliers may not capture the variation of regular observations (Hubert et al., 2005). However, by constructing the principal component (PC) space to be less sensitive to outlier profiles, dominant trends can be effectively revealed and we can distinguish contributions that cannot be seen with CPCA. Robust Principal Component Analysis (ROBPCA) is the statistical method used to achieve this (Hubert et al., 2005; Verboven and Hubert, 2005). The advantages of ROBPCA over CPCA were discussed in the statistical research of Filzmoser and Todorov (2011). Several studies have indicated that this method can also be successfully applied to geochemical data obtained from solid phases (Filzmoser, 1999; Filzmoser and Hron, 2008; Filzmoser et al., 2012), biosciences (Hubert and Engelen, 2004; Mauldin et al., 2008; Vezzaro et al., 2011), chemometrics (Hubert et al., 2002; Stanimirova et al., 2004), geography (Ghosh and Manson, 2008), and business (Todorov et al., 2011).

The purpose of this study was to demonstrate the spatio-temporal variability of groundwater chemistry in a highly permeable basaltic aquifer in the western part of Jeju Island, where an impermeable formation occurs beneath an agricultural field. The results of this study provide insight into the role of local geology on the spatio-temporal patterns in groundwater quality.

2. Site description

Jeju Island is located in the South Sea of South Korea and was formed by Pliocene-Quaternary basaltic-trachytic volcanism (Won, 1976). The highest point, Mount Halla (1950 m) is situated at the center of the island where forest and grassland are well preserved. The basalts covering most of the surface area of Jeju Island are characterized by highly permeable structures such as vesicles, clinker layers, interstices between lava flows, lava tunnels, and cavities. The basalt aquifer thus exhibits high hydraulic conductivity (average 234.3 m/day) and transmissivity (average 6904.3 m^2/day) (Won et al., 2006). Due to the permeable nature of the basaltic rocks, perennial streams are lacking and groundwater is the only source of fresh water. This permeability also makes the groundwater highly vulnerable to anthropogenic contamination.

This study focused on the Gosan area, located along the western coast of Jeju Island, which forms part of the Hankyung watershed (Fig. 1a). The climate of Gosan is characterized by strong winds and heavy precipitation during the summer season. For the last 30 years (1981–2010), average wind speeds were 7.0 m/s, which is about twice that of the entire island. Average annual precipitation was 1143 mm and average air temperature was 15.7 °C. Of the total annual precipitation in 2010 (1362 mm), ca 53% (723 mm) occurred during the rainy season (June–August) (http://www.kma.go.kr).

Fig. 1a shows the location, surface geology, and geologic cross-section of the Gosan area. The surface geology map shows that the Gosan Formation, Songaksan tuff, Dangsanbong tuff, and cinder cone occur in ascending order above the Kwanghaeak basalt. The Songaksan tuff forms the southern cliff of Mount Songak and is composed of sand-sized basaltic ash with gravel-sized basaltic and argillic rock fragments (Park et al., 2000). The Dangsanbong tuff and cinder cone consist of lapilli, ash, and sand. The tuff and cinder cone are extensively eroded to form a low hill in the northern part of the area (Park et al., 2000). The Kwanghaeak basalt has a glassy groundmass with subordinate phenocrysts of olivine and clinopyroxene (Park et al., 2000) and forms the main aquifer in the Gosan area. Regional groundwater flows from Mount Halla, which is located about 35 km ENE of Gosan (Koh et al., 2012b). The hydraulic conductivity of the aquifer beneath the western part of Jeju Island is reported to be 199.2 m/day (Won et al., 2005). Measurements of equipotential lines during the wet (August to September, 2002) and dry (March to April, 2003) seasons (Fig. 1b and c) show that regional groundwater flow is mainly directed from NE to SW (Jejudo, 2003).

The Gosan Formation (Seongsan Formation of Koh et al., 2012b) occurs in the western part of the study area and consists of impermeable clay and limonite-rich beds with a thickness of 1.0–1.5 m (Park et al., 2000). A perched aquifer is located above the Gosan Formation with a water table depth from 0.44 to 4.13 m below the surface (Koh et al., 2012b). Based on hydrochemical evaluation, Koh et al. (2012b) suggested that the shallow perched groundwater in the Gosan area is recharged through direct infiltration of precipitation through an agricultural field and thus is heavily contaminated by nitrate from synthetic fertilizers. The cross-section A–A′ in Fig. 1a shows that sand, tuffaceous sediments, basaltic fragments and mollusk shells of the Seogwipo Formation underlie the Kwanghaeak basalt in the study area and occur at depths of 37–100 m below sea level. Due to its low permeability and widespread distribution on Jeju Island, the Seogwipo Formation plays an important role in regulating the occurrence, distribution (including depth) and quality of the deep main aquifer on Jeju Island (Koh and Yoon, 1997; Won et al., 2005; Won et al., 2006).

The land use map (Fig. 2) shows that the land surface of the study area is extensively used for agriculture. Two rotations of crops are grown per year, involving the use of abundant synthetic fertilizers. The annual chemical fertilization rate in the area is very high (627.9 kg-N/ha) and varies between summer and winter seasons. Nitrogen fertilizers of 81.5 kg-N/ha on average are applied from April to October for rice, beans and sesame, while very high fertilization (546.4 kg-N/ha) occurs from November to March for garlic, onions, radishes and cabbage (Koh et al., 2012b). This very high rate of fertilization causes a notable degradation in the quality of groundwater, especially that of perched groundwater (Oh et al., 2010).

3. Materials and methods

3.1. Sample collection and physicochemical analysis

A total of 152 groundwater samples were collected in 2010 from 15 pre-existing wells during monthly sampling from January to September, with the exception of May. Well depths ranged from 70 to 118 m below the surface (Table S1). Several well volumes of groundwater were purged prior to sampling and the collected samples were filtered using 0.45 μm membrane filters and stored in pre-acid washed 60 ml HDPE bottles before analysis. Samples for cation analysis were acidified to pH < 2 using ultrapure nitric acid. The pH and EC were measured with portable electrodes that were