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Role of oxbow lakes in controlling redox geochemistry of shallow groundwater under a heterogeneous fluvial sedimentary environment in an agricultural field: Coexistence of iron and sulfate reduction

Byoung-Young Choi [a,b,*], Seong-Taek Yun [b], Kyoung-Ho Kim [b]

[a] Geologic Environment Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, South Korea
[b] Department of Earth and Environmental Sciences and Green School, Korea University, Seoul 136-701, South Korea

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ABSTRACT

This study aimed to extend the knowledge of the vertical distribution of redox conditions of shallow groundwater in heterogeneous fluvial sediments near oxbow lakes. For this study, we revisited the study area of Kim et al. (2009) to examine the redox zoning in details. Three multi-level samplers were installed along a flow path near two oxbow lakes to obtain vertical profiles of the subsurface geology and hydrochemical and isotopic data ($\delta^{18}O$ and δD of water, $\delta^{15}N$ and $\delta^{18}O$ of nitrate, and $\delta^{34}S$ of sulfate) of groundwater. Geologic logging showed that characteristics of the heterogeneous subsurface geology are closely related to the pattern of vertical redox zoning. Hydrochemical data in conjunction with nitrogen and sulfur isotope data show that the redox status of groundwater near oxbow lakes is controlled by denitrification, iron reduction, and sulfate reduction. The oxidizing condition of groundwater occurs in the sand-dominant alluvium located in the up-gradient of oxbow lakes, whereas the reducing condition accompanying denitrification, iron reduction, and local sulfate reduction is developed in silt-rich alluvium in and the downgradient of oxbow lakes. The occurrence of sulfate reduction was newly found in this study. However, the vertical profiles of redox-sensitive parameters show that iron reduction and sulfate reduction occur concurrently near oxbow lakes, although the measured redox potentials suggest that thermodynamic conditions are controlled by the stability of Fe^{2+}/Fe-oxides. Therefore, this study shows that the redox condition of groundwater in the iron-rich zone should be carefully interpreted. For this purpose, depth-specific sampling and careful examination of sulfur isotope data will be very useful for identifying the redox processes occurring in the zone with overlapping iron reduction and sulfate reduction in heterogeneous fluvial sediments.

1. Introduction

The redox process controls the behavior and fate of groundwater contaminants originating from either anthropogenic or natural sources (Barcelona et al., 1989; Appelo and Postma, 1999; Christensen et al., 2000; Biswas et al., 2011; Kumar and Riyazuddin, 2012; Hinkle and Tesoriero, 2014; Kim et al., 2014) and generally occurs in a well-known sequence in the order of oxic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis (Chapelle, 2001). The concentrations of NO_3^- and SO_4^{2-} in alluvial groundwater have increased worldwide in the few past decades because of the extensive use of fertilizers and manures, which adversely affect aquatic ecosystems and human health (US EPA, 1995; Trettin et al., 2002). Many studies have also demonstrated that NO_3^- and SO_4^{2-} can be reduced by denitrification and sulfate

* Corresponding author at: Geologic Environment Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, South Korea.
E-mail address: choiby@kigam.re.kr (B.-Y. Choi).

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reduction in the groundwater environment (Hiscock et al., 1991; Pauwels et al., 2000; Massmann et al., 2003; Choi et al., 2011). Even so, redox processes may increase the concentrations of undesirable byproducts, such as Fe^{2+} and H_2S (McMahon and Chapelle, 2008). Thus, for the management of groundwater quality, it is crucial to better understand the redox chemistry occurring in aquifers.

Several studies have reported that shallow alluvial groundwater of South Korea has been severely degraded by NO_3^- and SO_4^{2-} due to over-fertilization and manure application in agricultural fields (Min et al., 2003; Chae et al., 2004; Choi et al., 2007; Kim et al., 2008; Kim et al., 2009; Choi et al., 2011; Kim et al., 2014, 2015). Among these studies, a few researchers have noted that redox processes are largely controlled by the geologic properties (i.e., sedimentary environments) of the alluvial aquifer; in particular, aquifers containing organic-rich silt layers are favorable environments that facilitate reducing conditions (Min et al., 2003; Chae et al., 2004; Kim et al., 2008; Kim et al., 2009; Choi et al., 2011; Kim et al., 2014). These observations agree well with the other studies on the spatial distribution of redox conditions in relation to the variability of geologic and geochemical properties in aquifers (Smith et al., 1991; Starr and Gillham, 1993; Robertson et al., 1996; Hill et al., 2000). In particular, Kim et al. (2009) used the factorial kriging method to understand the spatial control of nitrate distribution in shallow groundwater based on hydrochemical data that were obtained from 45 shallow irrigation wells in the Osong area of South Korea. These authors reported major findings as follows: 1) a dramatic spatial change of redox chemistry occurs in alluvial groundwater, ranging from denitrification and iron reduction, and 2) redox zoning occurs restrictedly in a small area near the oxbow lakes, around which organic-rich silt is typically deposited. However, Kim et al. (2009) did not examine the vertical distribution of redox zoning. Therefore, we revisited this area to carefully re-examine the redox processes.

The main objective of this study is to better understand the spatial control of the redox conditions in heterogeneous sedimentary environments near oxbow lakes. For this study, we installed three multi-level samplers (MLSs) to obtain the vertical profiles of hydrochemical and isotopic data in conjunction with subsurface geology because MLSs can provide better insight into the depth-dependent redox chemistry (Tayler et al., 2006; Choi et al., 2011; Kim et al., 2014). The results of this study would aid better understanding of the geologic control of the redox process in heterogeneous alluvial sedimentary environments, which is important for the better management of agricultural contamination and for the successful application of artificial recharge technology in an alluvial setting.

2. Study area

The study site is located in the Osong area, where a fluvial plain developed between the Miho and Jocheon Streams of the Kum River Watershed, South Korea (Fig. 1). The climate condition of the study area is typical of temperate monsoon regions. During the past three decades, the annual averages of temperature and precipitation were 13 °C and 1300 mm, respectively. Approximately 70% of the annual precipitation occurs in a monsoonal period from June to August. This area is widely used for the cultivation of paddy rice and vegetables, with the use of shallow groundwater for irrigation purposes (Kim et al., 2009).

In this area, there are two oxbow lakes with opposite directions (Fig. 1). The available topographic maps of different publication years showed channel relocation in the area between 1923 and the present (Kim et al., 2009). Alluvium in the area is highly variable in texture because of the successive change of sedimentary environments due to the dynamic channel relocation; the sand-dominant layers represent the depositional facies in channels (i.e., point-bar sedimentary facies), whereas the silty layers represent the deposition in floodplain environments. Surface sediments near the oxbow lakes typically consist of fine-grained silt (Kim et al., 2009). Measurements of piezometric levels indicate the general groundwater flow toward the Miho Stream (Fig. 1). However, as suggested by the narrow piezometric contours near the two oxbow lakes, the groundwater flow is retarded there (Kim et al., 2009). More-detailed site descriptions are available from Kim et al. (2009).

3. Material and methods

3.1. Sampling and geochemical analyses

For the depth-specific groundwater sampling for this study, three sets of multi-level samplers (MLSs; OS-1, OS-2, and OS-3) were installed in paddy fields around two oxbow lakes. The locations of the MLSs were determined based on the groundwater flow and the locations of the two oxbow lakes in the study area (Fig. 1). The sampler OS-1 was installed at the downgradient site of groundwater flow adjacent to the current channel of Miho Stream (Fig. 1). Therefore, OS-1 is appropriate for examining the quality of groundwater finally discharging to the stream. The sampler OS-2 was located just downstream of the oxbow lakes (Fig. 1) to examine the biogeochemical roles of silt-dominant sediments around oxbow lakes. The sampler OS-3 was located at the upgradient site in the study area and on the locality of an old (from approximately 1923) oxbow lake (Fig. 1); thus, OS-3 was drilled within a paleo-channel and aimed to examine the groundwater quality as influenced by current agricultural contamination. The depths of each sampler and sampling ports are summarized in Table 1 and Fig. 2. During borehole drilling, alluvial sediments were recovered using PVC pipes for geologic logging, although coarse sandy sediments were very difficult to recover as a core (in this case, suspended materials outflowing with drilling fluids were sampled). After drilling, a bundle of 2.5-cm-diameter PVC pipes and 0.5-cm-diameter polyethylene (PE) tubes of different lengths were inserted into each borehole, and the boreholes were backfilled with sand. All of the pipes and tubes had a 15-cm-long slotted tip that was wrapped with a stainless steel screen for water passage and sampling. The PVC pipes were also used to measure groundwater levels.

A total of 36 samples of alluvial groundwater were collected for this study from the three MLSs with a peristaltic pump during two sampling campaigns in July 2003 (rainy season) and May 2004 (dry season). Prior to sampling, the groundwater levels were measured, and the groundwater was purged until the temperature and electrical conductivity (EC) were stabilized. The temperature, pH, Eh (redox potential), EC, and