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Hydrogeochemistry of alluvial groundwater in the Osong area, Cheongju: natural attenuation of nitrogen compounds

Gi-Tak Chae, Seong-Taek Yun*, Kyoung-Ho Kim, Chul-Ho Heo, Kangjoo Kim[1], Chul-Woo Rhee[2], Hyoung-Soo Kim[3]

Dept. of Earth & Environ. Sci., Korea Univ.; [1]Kunsan Univ.; [2]Chungbuk National Univ.; [3]Korea Water Resources Co.

*E-mail: styun@korea.ac.kr

Fig. 1a. Present-day topography of the study area (Osong-Ri, Kangwoe-Myeon, Chungcheongbuk-Do)

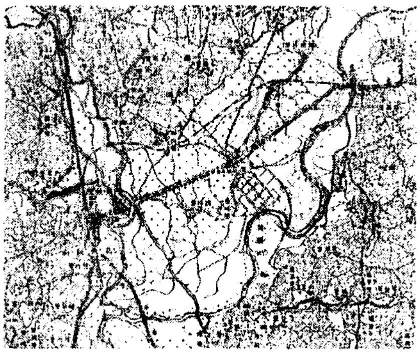

Fig. 1b. Topography of the study area in 1940s

Hydrogeochemical and hydrolgeological studies have been performed in September and November of 2001 and June of 2002, in order to understand the nitrate behaviors in a riverside, shallow alluvial groundwaters of the Osong area near Cheongju (Fig. 1a). Because of the intensive agricultural activities, large population, and excessive pumping of groundwater in the area, nitrate contamination has been expected; this was the background of this study.

The meandering Miho stream, a tributary of the Kum river, has shifted the locality after 1940's, as indicated by comparing topographic maps in different times (Fig. 1). Such migration of the stream leaved two large oxbow lakes in the area and possibly caused the spatial heterogeniety of aquifer materials. Because these two oxbow lakes are presently parallel and adjacent to each other, it can be considered that the formation time was different each other. A silt layer located just below the surface agricultural soil varies in thickness and connectivity (Fig. 2). A NE-SW GPR profile of the study area (Fig. 3) also shows that sediment layers in the area are significantly discontinuous. Although groundwater levels were possibly disturbed by long drought and intensive irrigation in the fall season of 2001 or by heavy rainfall in the summer of 2002, piezometric data indicate that groundwater generally flow toward the present Miho stream (Fig 4). The area where two oxbow lakes are located can be considered as the so-called 'riparian zone', where natural attenuation of nitrogen compounds., i.e. denitrification, preferentially takes place. Thus, such areas would be very important for clean water supply, especially through bank filtration and/or underground dam construction.

A total of 54 groundwater samples in the study area were collected for cation, anion, and isotope analyses. In 28% of the samples, NO_3-N concentrations exceeded the drinking water standard (10 mg/L). The collected waters are clustered into two groups on the Piper's diagram: Ca-HCO_3 type and Ca-SO_4(-NO_3) type (Fig. 5). The data of Eh, DO, DOC, EC, Ca, K, Mg, Na, SO_4, and NO_3 for the Ca-SO_4(-NO_3) type waters were higher than those of the Ca-HCO_3 type waters. In contrast, Fe, Mn, and HCO_3 concentrations were higher in Ca-HCO_3 type waters. It is noteworthy that samples with low NO_3 concentrations among Ca-HCO_3 type waters are distributed charateristically in the vicinity of the two oxbow lakes (Fig. 6).

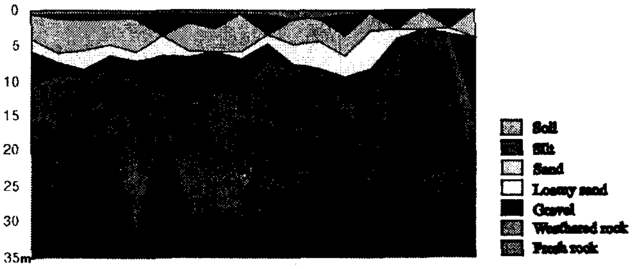

Fig. 2. A N-S-trending cross section of the study area, showing the geology of alluvium.

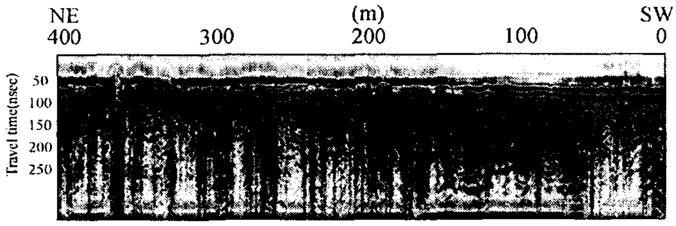

Fig. 3. A NE-SW-trending GPR profile of the study area

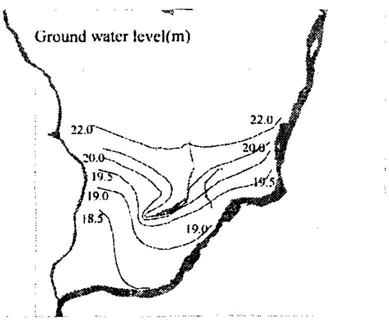

Fig. 4. Contour map of the measured groundwater levels (m; a.s.l.)

In the agricultural area, NO_3 can be originated from mineralized N-fertilizer and livestock manure. These two non-point sources likely pollute the groundwater because paddy field and pasture are ubiquitous in the study area. However, the relationship between NO_3 and K concentrations (Fig. 7A) suggests that the most plausible source of NO_3 in the area is manure rather than N-fertilizer, because application of mineralized fertilizer generally cause a parallel increase of dissolved N and K. We are currently conducting N isotope analysis to identify the nitrate source(s).

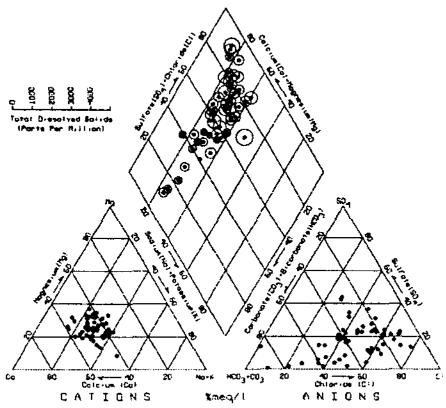

Fig. 5 Piper diagram for alluvia groundwaters in the study area

An abrupt change of NO_3 concentration was observed around the oxbow lakes, ranging from 123 mg/L in the fall of 2001 and 230 mg/L in the summer of 2002 to <0.1 mg/L in the fall of 2001 and 1.2 mg/L in the summer of 2002. Assuming that groundwater flow is continuous in the area, NO_3 can be eliminated by the hydrogeochemical processes within aquifer, which include dilution, biological uptake, denitrification, and nitrogen reduction. Low NO_3 concentrations occurred in the samples with low Eh values (Fig. 7B). Starr and Gillham

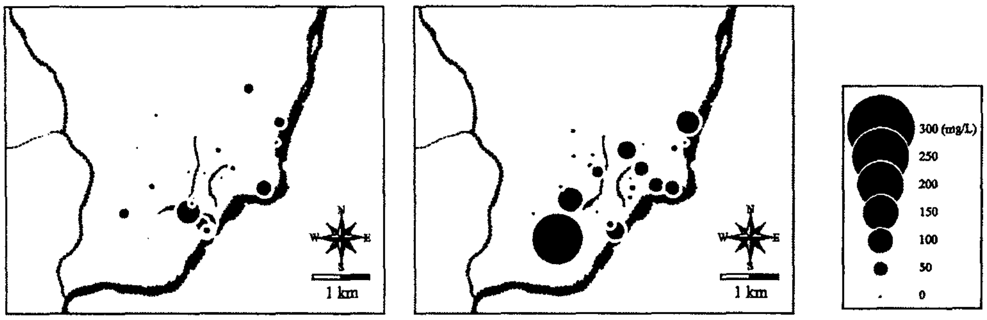

Fig. 6. The distribution of nitrate concentration
(left: summer of 2002; right: fall of 2001)

(1993) suggested that denitrification takes place in sub-oxic conditions (DO <2 mg/L, Eh <200 mV). For NO_3-poor samples in the study area, measured DO (mean 0.8 mg/L) and Eh

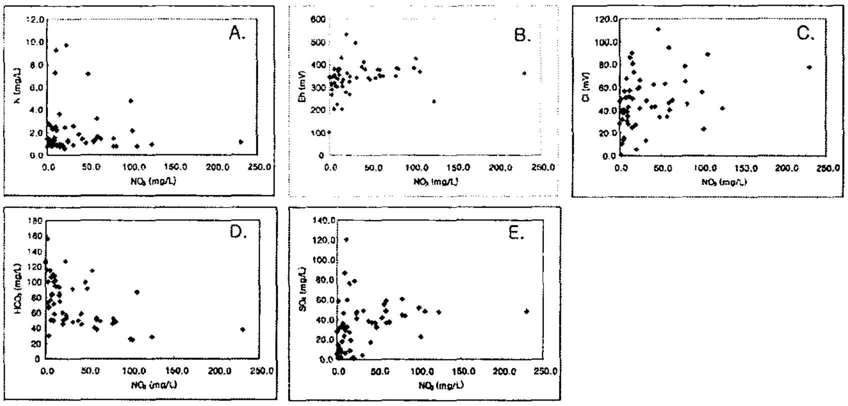

Fig. 7. The relationships between NO_3 concentration and other hydrochemical parameters related to th denitrification

(mean 135 mV) values fell in the suggested range for denitrification. On the other hand, most of the samples are plotted away from a dilution line in a NO_3 versus Cl diagram (Fig. 7C). Consequently, NO_3 concentration in groundwaters of the study area is largely controlled by redox conditions and are decreased by denitrification.

Common electron donors in denitrification include organic carbon, reduced sulfur, and ferrous iron. In other words, denitrification can take place either by the oxidation of organic carbon mediated by heterotrophic bacteria:

$$5CH_2O + NO_3 + 4H^+ = 5CO_2 + 2N_2 + 7H_2O$$

or by the oxidation of reduced sulfur and ferrous iron mediated by autotrophic microorganisms:

$$5FeS_2 + 14NO_3 + 4H^+ = 7N_2 + 10SO_4^{2} + 5Fe^{2+} + 2H_2O$$

$$5Fe^{2+} + NO_3 + 12H_2O = 5Fe(OH)_3 + 0.5N_2 + 9H^+$$

Measured HCO_3 concentrations were lower in NO_3-poor samples (Fig. 7D), likely indicating that heterotrophic process is predominant in the study area. Although direct evidences of sulfate reduction, i.e., noticeable amounts of H_2S and high $\delta^{34}S$ values of sulfate, have not been acquired, the lower SO_4 concentrations in more NO_3-poor samples (Fig. 7E) also suggest that autotrophic processes of denitrifcation cannot be a successful explanation.

In summary, the reducing zone where denitrification occurs is preferentially located around the two oxbow lakes. This zone can be regarded as 'riparian (buffer) zone'. In recent years, the term 'riparian zone' has come to include not only the river banks but also a wider strip of land on either side of the channel (Malanson, 1993); the flood plain is usually coincident with this more broadly defined area. We should note that riparian zone is the optimum site of bank filtration and underground dam construction. The present study is still ongoing to well understand the natural attenuation of contaminants such as NO_3, Fe, Mn, etc. in relation to the formation of reducing riparian zone. The results of this study can be applied to the water use technology such as bank filtration and underground damming. In Korea, this study is the first attempt to integrate related approaches, i.e., hydrology, hydrogeochemistry, geophysics, and sedimentology, to elucidate the hydrogeological and hydrochemical processes in an alluvial aquifer.