Hydrogeochemistry of shallow groundwater in a small catchment area, Cheonan, Korea: Emphasis on redox condition and nitrate problem

Kyoung-Ho Kim[1], Seong-Taek Yun[1], Gi-Tak Chae[1], Byoung-Young Choi[1], Kangjoo Kim[2], Chul-Woo Lee[3], Hyoung-Soo Kim[4]

Introduction

Shallow groundwater systems are highly vulnerable to anthropogenic contamination and are characterized by a variety of redox condition. The redox state is a key parameter to control the nitrate contamination which is related to nitrification or denitrification processes. In relation to the control of nitrate problem, it is very important to understand the source, transport and fate of nitrogen compounds in a groundwater system. There are two major mechanisms causing denitrification: 1) reduction by heterotrophic microorganisms and the simultaneous respiration of CO_2 from oxidation of organic matter and 2) reduction by chemo-autotrophic respiration accompanying oxidation of reduced sulfur. However, it is usually difficult to elucidate successfully the appropriate denitrification mechanism, due to the heterogeneity of alluvial aquifer (Min et al., 2003). Therefore, an integrated hydrogeologic and hydrogeochemical study is generally required.

In order to understand the redox process and associated nitrate problem in a shallow alluvial aquifer system, we performed a hydrogeologic and hydrogeochemical study in the Cheonan area. In the area, elevated levels of NO_3^- (max. 77.6 mg/L) were observed owing to agricultural activity. However, the nitrate concentrations were locally found to be attenuated down to <1.0 mg/L. Such pattern spatially coincided with the change of redox condition and indicated that denitrification was the most plausible process for the nitrate removal.

Study area and hydrogeology

Fig. 1 shows the sites of sampling of irrigation well groundwaters (about 15 to 25 m below the land surface) in this study. The distribution of nitrate concentration is also shown. In many sites, nitrate levels exceeded the drinking water quality standard. In specific sites, however, the concentrations were attenuated to <1 ppm. Therefore, we have chosen this area in this study to elucidate the behavior of anthropogenic nitrogen
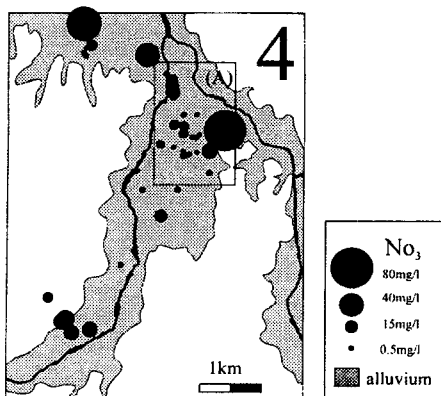
Fig. 1 Sampling localities and distribution of nitrate concentration in alluvial groundwater of Cheonan area. Box (A) indicates the site of detailed study
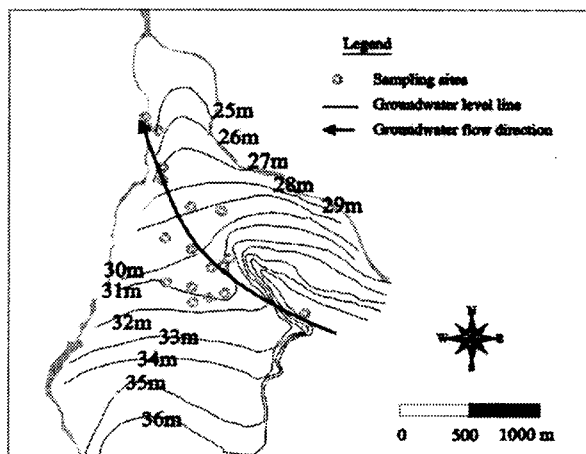

Fig. 2 Distribution of sampling wells and groundwater level (a.s.l.)

compounds. Fig. 2 shows the distribution of groundwater levels (a.s.l.) and also shows that sampling locations are arranged along the preferential path of groundwater flow.

The Precambrian banded biotite gneiss occurs as a basement in the study area. Alluvial sediments are about <20 m thick and are mainly composed of coarse sand, gravel and unconsolidated rock fragments (Fig. 3). A thick silt-rich layer occurs above the aquifer and seems to act as an impermeable layer. The groundwater table is generally located at 4-5 m depth and becomes gradually deeper toward south (Fig. 2). Groundwater recharge in the area occurs at topographically high land (Fig. 2). Pollutants of nitrogen compounds are originated from animal manure in poultry farming at such recharge zone and migrate downward through local flow system. However, direct infiltration of rain water occurs only restrictedly at the area without a silt layer. Fig. 4 illustrates the local flow path of groundwater and nitrate in the study area.
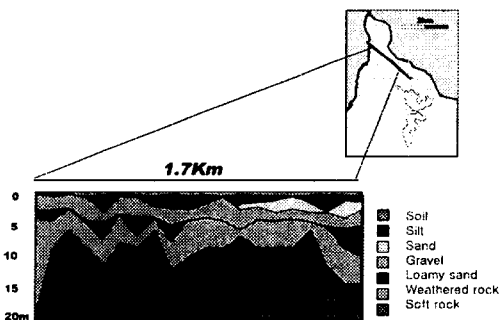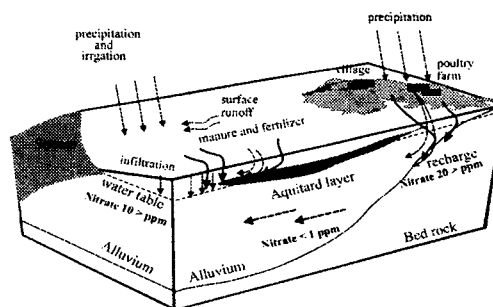

Fig. 3 Geologic profile of the study area.

Fig. 4 A schematic model of hydrogeology and contaminant transport in the study area.

Hydrogeochemisty

Fig. 5 shows the spatial variations of the concentrations of redox-sensitive species such as nitrate, sulfate, iron, manganese and dissolved organic carbon (DOC), as well as of the related physicochemical parameters such as pH, Eh and dissolved oxygen (DO) along the local flow path. In the recharge region, shallow groundwaters contain high concentrations of nitrate, presumably as an influence of a point source effluent from poultry farming and sewage. Passing the recharge region, however, the nitrate levels are attenuated abruptly. In such nitrate-depleted zones, geochemical environments are typically anoxic, as indicated by low Eh and DO values. The local anoxic conditions are possibly formed by biogeochemical processes which cause the consumption of oxidants (nitrate and dissolved oxygen) by substrates (organic carbon and/or pyrite) in the sediments. It is also noteworthy that in such anoxic zones sulfate concentrations generally increase. This result may indicate that the dominant reaction controlling the nitrate attenuation is likely an autotrophic denitrification that uses reduced sulfur (likely pyrite) in sediments.

Largely in the place where the aquifer is overlaid by unsaturated zone with a thick silt layer, however, the groundwater also can be protected from the infiltration and contamination of nitrate. Thus, local infiltration of nitrate in agricultural land is possibly restricted in the place where the silt layer is disconnected. Therefore, we consider that after significant attenuation of nitrate in anoxic conditions, nitrate can be available again through direct infiltration where the geochemical environments rebuild an oxic zone as dissolved oxygen easily infiltrates through the unsaturated zone.

Variations of chlorine concentrations show that hydrologic mixing process also occurs
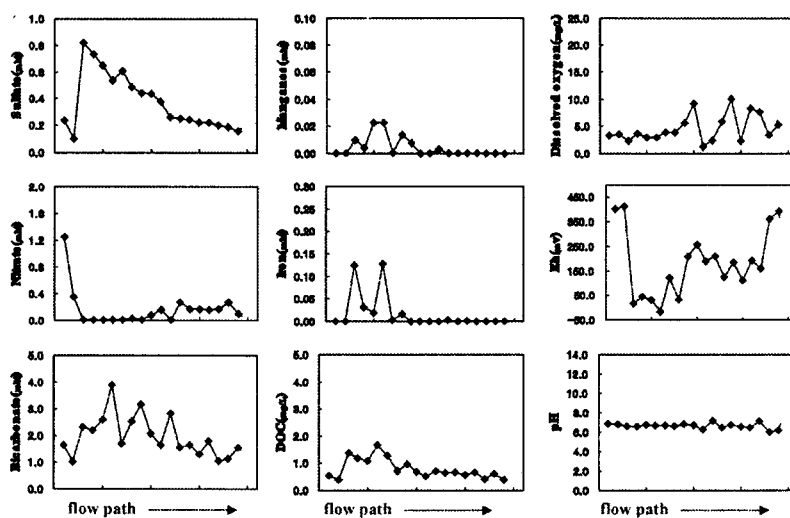

Fig. 5 Variations of the concentrations of redox-sensitive chemical species and of physicochemical parameters in groundwaters along a local flow path
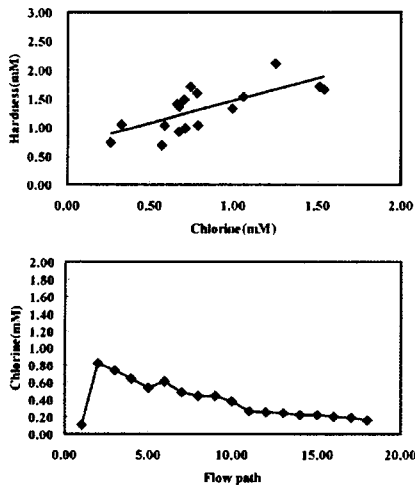
Fig. 7 Relationships among nitrate, sulfate, and chlorine concentrations in an alluvial aquifer of the study area

Fig. 6 Binary mixing of groundwater in the study area, based on the variation of chlorine concentration along the local flow path.

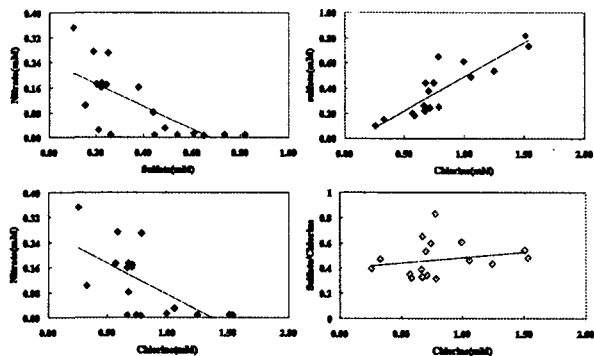along the hydraulic gradient (Fig. 6), causing dilution of groundwaters. The dilution effect makes it difficult to estimate the role of denitrification. In spite of the dilution process, however, concentrations of nitrate tend to increase along the flow path. Fig. 7 also suggests that sulfate reduction does not proceed in the study area; thus, the sulfate is formed through denitrification reaction and its concentration is only affected by hydrologic mixing. In summary, we consider that denitrification reaction largely controls the distribution of nitrate in the study area.

References

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