

Hydrochemistry of an alluvial aquifer in the Cheonan area: role of the pyrite oxidation on denitrification

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Abstract

To examine the denitrification process in an alluvial aquifer in the Cheonan site, hydrological and hydrogeochemical studies were carried out. Elevated levels of NO_3 (maximum 77.6 mg/L) were observed in shallow groundwaters of the area, as a result of poultry and agricultural activity. However, the nitrate concentrations were found to be consistently attenuated down to very low levels (<1.0 mg/L). The abrupt removal of nitrate coincided with the pattern of redox change and indicated that denitrification is the most plausible process. The hydrochemistry and mass balance approach using geochemical modeling (phreeqc 2.0) and redox chemistry indicated that chemo-autotrophic denitrification via pyrite oxidation is the key process to control the nitrate attenuation in the study area.

Introduction

There are two major mechanisms causing denitrification: 1) nitrate reduction by the heterotrophic microorganisms and the simultaneous respiration of CO_2 from the oxidation of organic matter and 2) nitrate reduction by chemo-autotrophic respiration accompanying oxidation of reduced sulfur. In general, the primary processes of nitrate attenuation within alluvial aquifers are generally considered to be denitrification, vegetable uptake, or dilution. Enormous studies on denitrification in alluvial aquifers have been performed throughout the world, it is still very difficult to successfully elucidate the appropriate denitrification mechanism, due to the heterogeneity of alluvial aquifer and the difficulty of access to the subsurface aquifer materials (Min et al., 2002). This study was performed to understand the denitrification process in an alluvial aquifer in the Cheonan area.

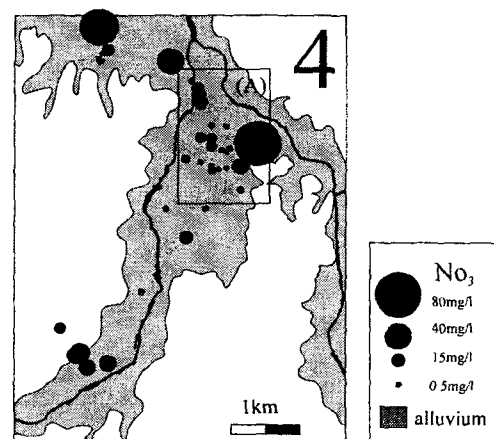


Fig. 1 Distribution of nitrate in alluvial groundwaters in the Cheonan area.

Box "A" indicates the site of detailed study

Selection of study area

Fig. 1 shows the sampling site in the study area, together with the distribution of nitrate concentration in shallow, irrigation well groundwaters (about 15 to 25 meters deep below the land surface). In many sites, nitrate levels approach or exceed the irrigation water quality standard (10 ppm). However, in specific sites the concentrations are greatly attenuated to very low levels (<1 ppm). Therefore, we have chosen this area to elucidate denitrification process in an alluvial aquifer.

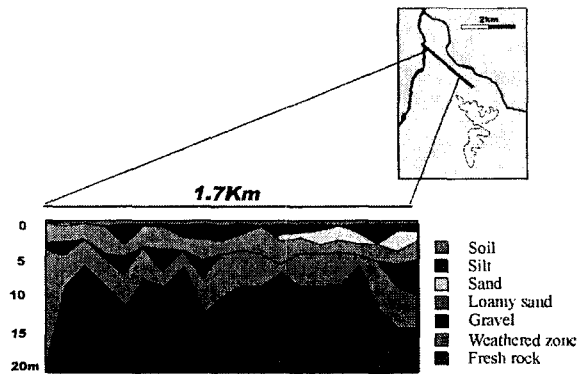


Fig.2 Geologic profile of the study area

Hydrogeology

The shallow aquifer in the study area forms within alluvial sediments (<20 m thick) which are composed of coarse sand, gravel, and weathered soil (Fig. 2). The Precambrian, banded biotite gneiss occurs as basement in the area. An impermeable, silt-rich layer characteristically exists near the land surface and acts as an aquitard (Fig. 2). The water table is generally located at 4-5 m below the land surface, and is gradually lowered toward south (Fig. 3). Groundwater recharge in the area likely occurs at topographic high land (Fig. 3). This recharge zone is affected by nitrogen compounds originated from animal manure from poultry farming. Therefore, it is likely that nitrogen compounds derived from animal manure migrates downward through local flow system. However, direct infiltration of rain water also seems to occur at the area without a silt layer. Thus, a local recharge of chemical fertilizer and manure also possibly occurs in such area, causing contamination of the groundwater. Therefore, it is likely that nitrogen compounds derived from animal manure migrates

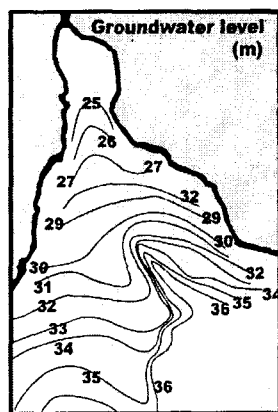


Fig. 3 Contour map of groundwater levels (a.s.l.)

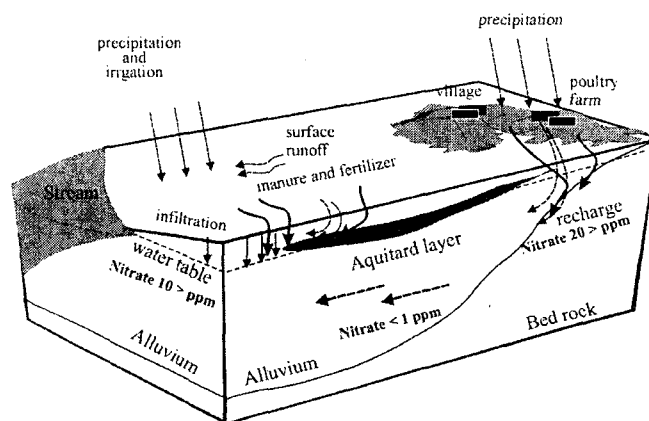


Fig. 4 A schematic model of hydrologic setting and contaminant transport in the study area

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characteristic hydrogeologic environments in the study area make a sequence of reaction and solute transport to be oriented largely in the direction of groundwater flow. Fig. 4 depicts both the local groundwater flow path and the recharge and transport of manure-originated nitrate in the study area.

Hydrogeochemistry

Fig. 5 shows the distribution of the concentration of redox sensitive chemical species (nitrate, sulfate, iron, manganese, dissolved organic carbon) and related physicochemical parameters (pH, Eh, dissolved oxygen) along the local flow path. In the recharge region, shallow groundwaters contain high concentrations of nitrate, presumably as a result of the

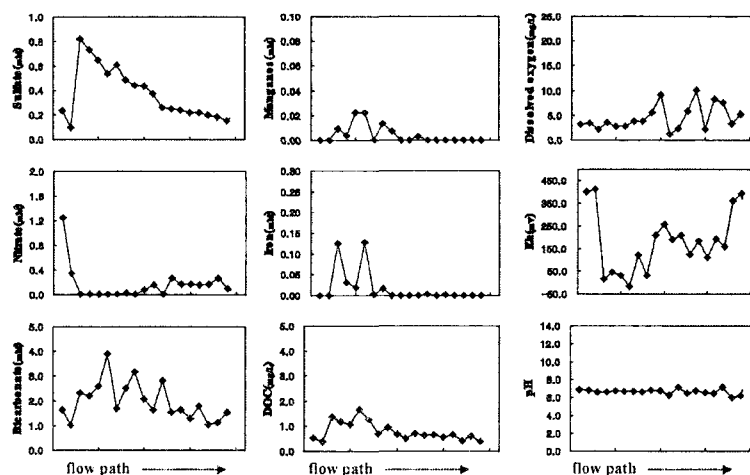


Fig.5 Variations of the concentration of redox sensitive species and the physicochemical parameters in shallow groundwaters along the local flow path

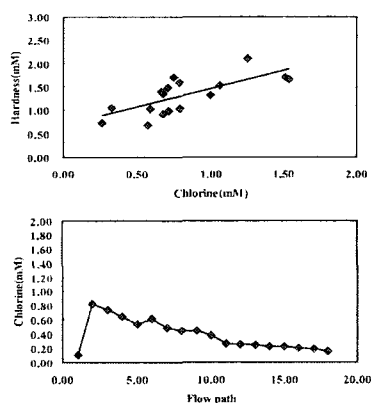


Fig. 6 Binary mixing model for groundwater in the study area, based on chlorine concentrations along the local flow path

influence of a point source effluent from poultry farming and sewage. Passing the recharge region, however, nitrate levels are attenuated abruptly. In these nitrate depleted zones, geochemical environments typically become anoxic, as indicated by low Eh and DO values. Those 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 noteworthy that in such anoxic zones sulfate concentrations of groundwater increase. This suggests that the dominant reaction controlling the nitrate attenuation is the autotrophic denitrification that consumes reduced sulfur compounds (likely, pyrite) in sediments. In the place where the aquifer is overlain by a silt layer as an aquitard, the groundwater is probably protected from direct infiltration of nitrate. In other words, local infiltration of nitrate in agricultural land is restricted to the place where the aquitard is disconnected. Even after

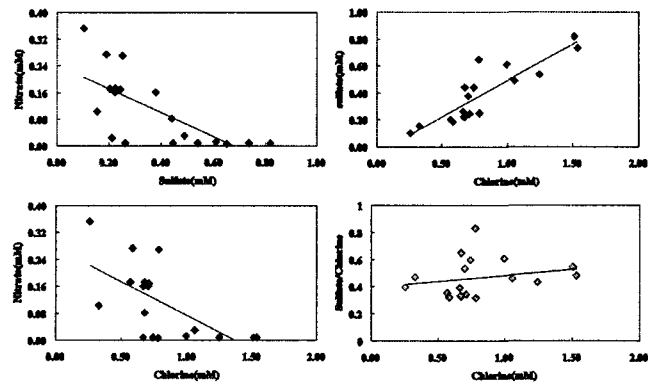


Fig. 7 Relationships among nitrate, sulfate, and chlorine concentrations in an alluvial aquifer of the study area

significant attenuation of nitrate in anoxic conditions occurs, therefore, nitrate may become available again through direct infiltration in agricultural land where geochemical environment of aquifer is locally rebuilt to an oxic state as dissolved oxygen infiltrates through the unsaturated zone. We consider concentrations of nitrate may increase again, due to local absence of a silt-rich aquitard.

Variations of chlorine concentrations also show that hydrologic mixing is advanced along the hydraulic gradient (Fig. 6), which causes dilution of groundwaters. This dilution effect makes it difficult to estimate the denitrification reaction. In spite of the dilution process, however, concentrations of nitrate increase slightly along the flow path. Fig. 7 also suggests that sulfate reduction does not proceed in the study area; and thus the concentrations of sulfate which formed through denitrification are only affected by hydrologic mixing. Detailed hydrochemical study on the products and substrates of redox reaction demonstrated that denitrification reaction occurs in the studied alluvial aquifer and largely controls the distribution of nitrate. We are conducting the analyses of ^{15}N and ^{18}O composition of nitrate and of plausible reducing agents (carbon and/or sulfur) in sediments.

References

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