

## Sources and Behaviors of Nitrate and Sulfate in Riverside Alluvial Aquifer

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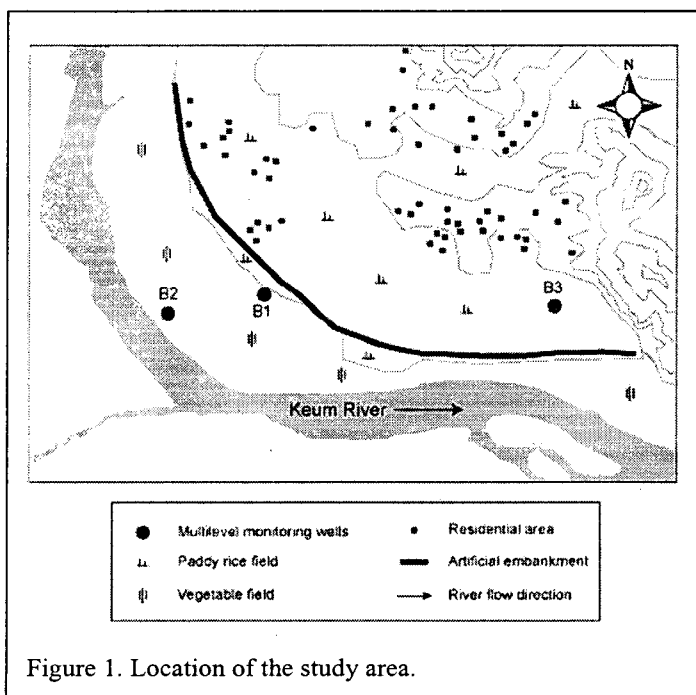
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### Introduction

Agricultural activities become an important cause of the deterioration of groundwater quality, because of the input of high concentrations of nitrate and sulfate into aquifer. Nitrate and sulfate are originated from various sources and their transformation is principally controlled by redox condition. Thus, the identification of the sources and biogeochemical cycles of them is very important for the management and preservation of groundwater. The objectives of this study are to elucidate the sources of nitrate and sulfate in riverside alluvial aquifer and to identify the transformation of those two species using stable isotopes. In addition, the control of redox condition in alluvial aquifer is discussed.

### Methods



For this study, three multi-level monitoring wells (MLWs) were installed in an alluvial aquifer at Buyeo area, Geum River watershed, Korea (Figure 1). Monitoring of the concentrations of cations (Na, K, Ca, Mg, Fe) and anions (Cl, HCO<sub>3</sub>, NO<sub>3</sub> and SO<sub>4</sub>) and stable isotopic compositions ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate, and  $\delta^{34}\text{S}$  of sulfate) were performed in 2002

### Results and discussion

#### Hydrogeochemistry

The vertical change of groundwater chemistry in the studied aquifer is shown in Figure 2. The hydrogeochemical data show that the water chemistry is clearly divided into two major parts with depth: oxic (upper) and sub-oxic (lower). The two different water zones are hydrologically and hydrochemically separated by the characteristic subsurface geology, especially the presence of low permeability units (silt). Especially, it is noticeable that sub-oxic groundwater has the lower concentrations of  $\text{NO}_3$  and  $\text{SO}_4$  than oxic groundwater, whereas Fe concentration increases in sub-oxic groundwater. However, the concentrations of Cl which can be considered as a conservative ion show the different variation with  $\text{NO}_3$  and  $\text{SO}_4$ . Thus,  $\text{NO}_3$  and  $\text{SO}_4$  are likely removed from groundwater by denitrification and sulfate reduction in sub-oxic zone. Reduction of iron oxides is the main cause of the increase of dissolved Fe in groundwater.

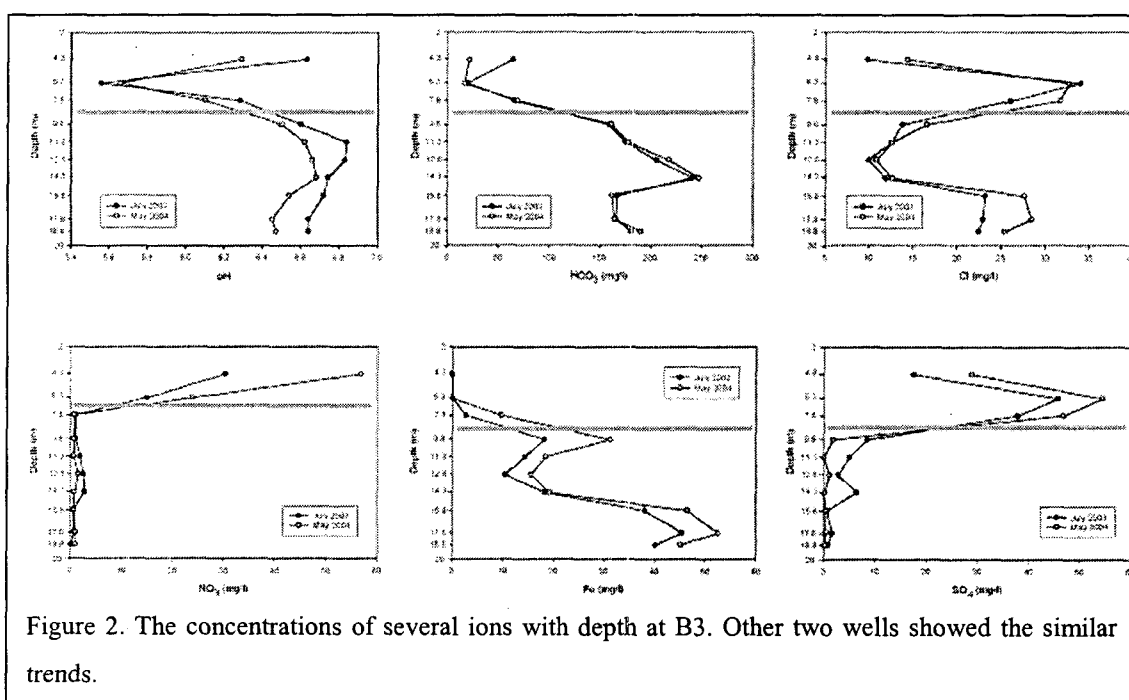


Figure 2. The concentrations of several ions with depth at B3. Other two wells showed the similar trends.

### Sources of nitrate and sulfate

The  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  data of nitrate indicate that nitrate in oxic groundwater is likely originated from manure and urea-containing fertilizer which are affected by nitrification (Figure 3). Our data also show that denitrification locally occurs in the studied area, resulting in the decrease of nitrate

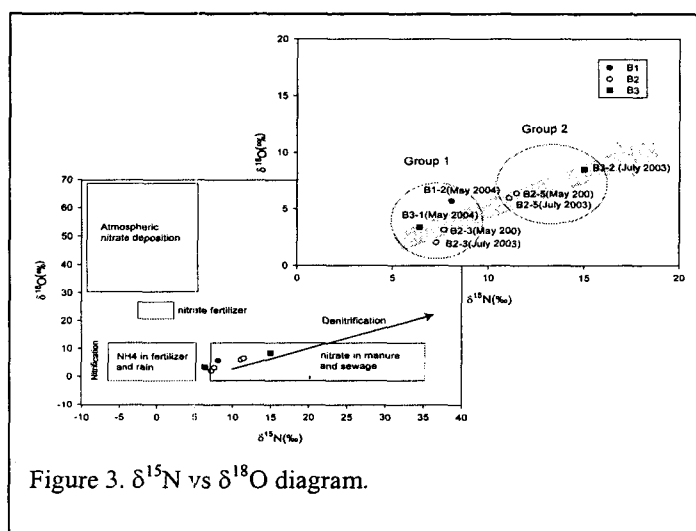


Figure 3.  $\delta^{15}\text{N}$  vs  $\delta^{18}\text{O}$  diagram.

concentration along with the increase of N and O isotopic composition. The  $\delta^{34}\text{S}$  values of sulfate suggest that sulfate is mainly originated from compound fertilizers and soil sulfur (for B2 and B3) and reduced inorganic sulfur (for B1) (Figure 4).

#### Redox condition and the iron and sulfate hydrochemistry

The  $\delta^{34}\text{S}_{\text{sulfate}}$  values of sub-oxic groundwater are highly increased with the concomitant decrease of sulfate concentration: up to 64.1‰ in B1, 5.6‰ in B2, and 43.2‰ in B3. This indicates the occurrence of microbial-mediated sulfate reduction in sub-oxic zone. However, as shown in Figure 2, the concentrations of dissolved iron steadily increase with depth, while sulfate is maintained at low concentrations with depth. This suggests that general redox sequence is maybe reversed in the study area. Figure 5 shows the stability of different Fe(III) oxides in a pH vs  $-\log[\text{Fe}^{2+}]$  diagram which was constructed for the reaction  $9\text{Fe}^{2+} + \text{SO}_4^{2-} + 20\text{H}_2\text{O} \leftrightarrow 8\text{Fe}(\text{OH})_3 + \text{FeS} + 16\text{H}^+$ . The sub-oxic groundwaters are plotted between the goethite and lepidocrocite lines. We suggest that sulfate reduction is a governing process in the studied aquifer where the stability of iron oxides is close to goethite and hematite.

#### Summary

The  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  data of nitrate indicates the sources of nitrate in oxic groundwater as a mixture of ammonia or urea-containing fertilizer and manure. The  $\delta^{34}\text{S}_{\text{sulfate}}$  values indicate that sulfate is mainly originated from fertilizers and soil S. In sub-oxic groundwater, the increased  $\delta^{34}\text{S}_{\text{sulfate}}$  values evidently indicate that sulfate is gradually removed by microbial mediated sulfate reduction. However, iron reduction does not occur in this study area. Such a reversed redox sequence may occur in the presence of stable iron oxides such as hematite and goethite in alluvial aquifer.

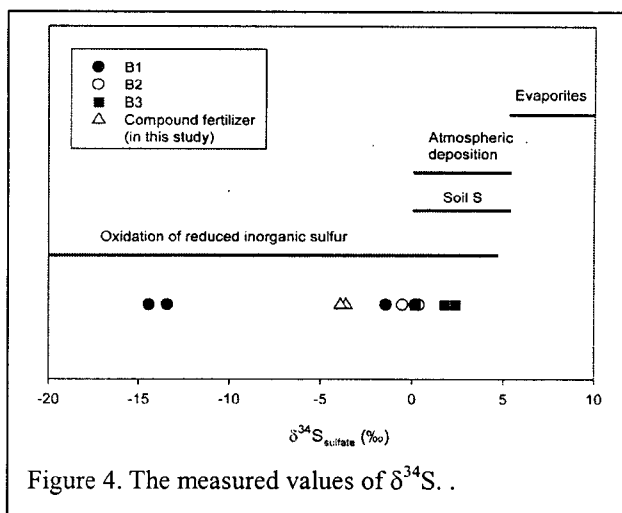


Figure 4. The measured values of  $\delta^{34}\text{S}$ .

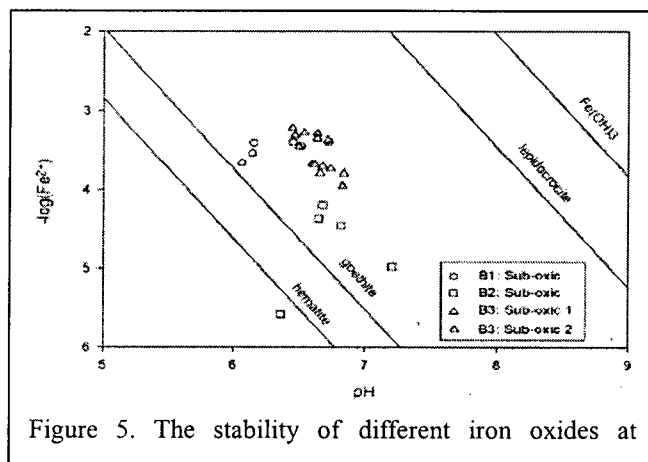


Figure 5. The stability of different iron oxides at