

## Hydrochemical behavior of agrochemicals in alluvial aquifer: geochemical modeling of nitrogen compounds

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In this study, we performed the inverse (mass balance) and forward (reaction) modelings for groundwaters from an alluvial aquifer at Buyeo (Fig. 1), in order to understand the observed hydrochemical change with a special emphasis on the behavior and fate of nitrogen compounds in agricultural land. Groundwaters were collected and analyzed in a dry season of 2001 and a wet season of 2002.

The collected groundwaters were hydrogeochemically and statistically classified into three groups (Fig. 2): highly contaminated by nitrate (Group I:  $\text{NO}_3$  mean = 194.7 mg/L in 2001 and 217.8 mg/L in 2002), moderately contaminated (Group III:  $\text{NO}_3$  mean = 58.4 mg/L in 2001 and 37.9 in 2002), and contaminated but naturally attenuated (Group II:  $\text{NO}_3$  mean = 0.9 mg/L in 2001 and 2.1 in 2002). Among the designated groups, Group I waters also showed the highest concentrations of Ca, Mg, Cl and  $\text{SO}_4$ , whereas pH and  $\text{HCO}_3$  were lowest. On the other hand, Group III waters showed the lower concentrations of Ca, Mg, Cl and  $\text{SO}_4$  but the higher concentrations of pH and  $\text{HCO}_3$  and therefore were considered to represent the hydraulically up-gradient groundwaters in the study area. Thus, the inverse and forward modelings were conducted to quantify the hydrochemical reaction(s) and pathway(s) for the generation of Group I waters from Group III waters.

The results of inverse and forward modelings showed that nitrification could release abundant acid and maintained low pH and  $\text{HCO}_3$  condition, which could overwhelm the acid buffering capacity (possibly due to dissolution of aquifer minerals and/or lime) of the aquifer. The nitrate-nitrogen isotope data also indicated that the nitrate in groundwaters was mainly originated from nitrogen fertilizers such as urea. As nitrification consumed a plenty of oxygen, the area of Group I waters was expected to be open to atmospheric oxygen (Fig. 3). Thus, the area of Group I waters is likely more porous and permeable than other areas, which was also expected by comparing the topography between 1923 and 2000 (Fig. 4). Furthermore, the observed expansion pattern of the nitrate-contaminated area during wet season (Fig. 5) also suggested that the source of nitrate pollution is spatially related to groundwater recharge in the study area. Therefore, we consider that agrochemical nitrogen compounds were oxidized near the agricultural land surface and then infiltrated to the groundwater system with recharging precipitation.

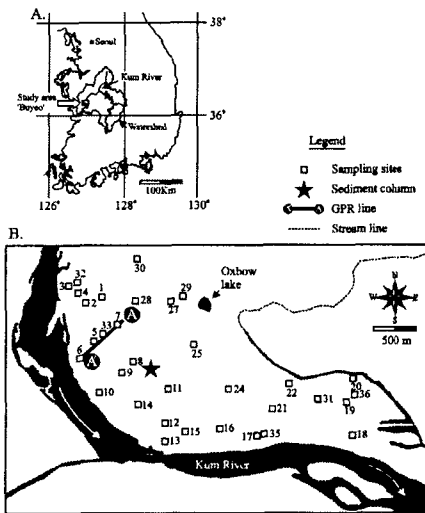


Fig. 1 The location of study area and the sampling sites

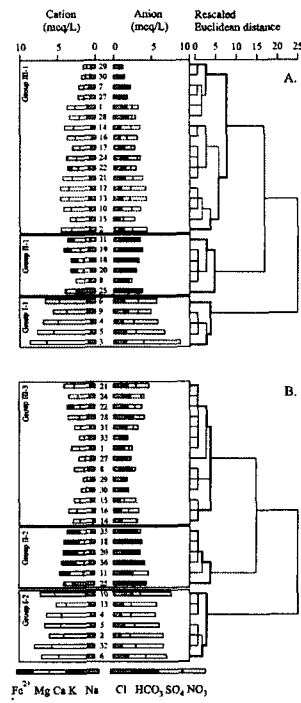


Fig. 2 The chemical compositions of groundwater groups.

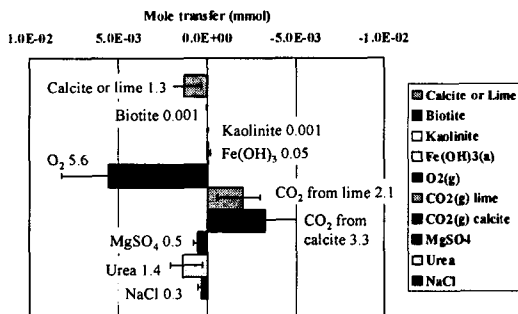


Fig. 3 The result of mass balance modeling explaining the nitrification from Group III to I waters.

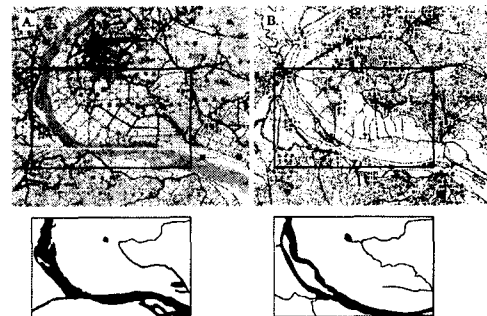


Fig. 4 The comparison of topography between 1923 and 2000.

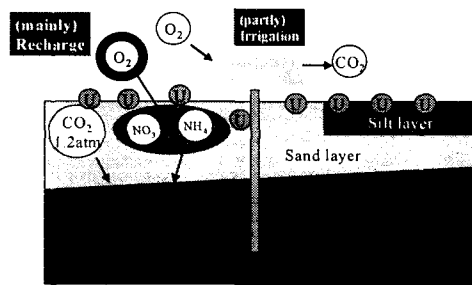


Fig. 5 Schematic diagram show the inflow of oxygen through sand rich sediments.

Such permeable alluvial strata along a riverside may have an advantage for filtering the quantity of river water in treatment of contaminated surface water, i.e., bank filtration. However, the oxic condition in this area also may seriously disadvantageous because of the vulnerability to nitrate contamination. Therefore, we consider that careful examination is needed to balance the two problems (water quantity vs water quality) in designing the water supply plan.

Denitrification by oxidation of organic carbon was likely the dominant reaction for the generation of Group II waters, which could increase the pH and  $\text{HCO}_3^-$  concentration and could attenuate nitrate in groundwater. However, the denitrification process also form an anoxic condition of the aquifer and may generate appreciable concentrations of dissolved Fe and Mn to give improper odor and color to the water. We also have performed the inverse and forward modelings to elucidate the hydrochemical processes controlling the behaviors of sulfur, carbon, and nitrogen (Fig. 6). The carbon and sulfur isotope data suggested that organic carbon was likely a prevailing reducing agent in the study area (Fig. 7), which resulted in the reduction of sulfur to hydrogen sulfides (Fig. 8). This explanation agreed well the results of mass balance and reaction modelings.

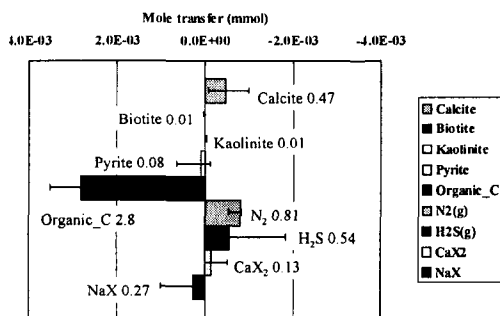


Fig. 6 The result of mass balance modeling explaining the reduction of nitrate and sulfate by organic carbon.

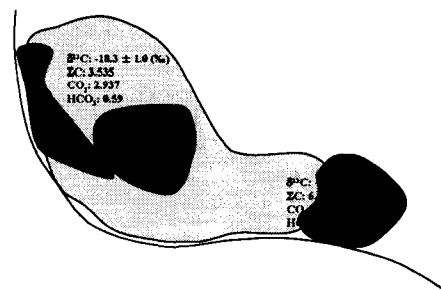


Fig. 7 The result of carbon isotope mass balance modeling.

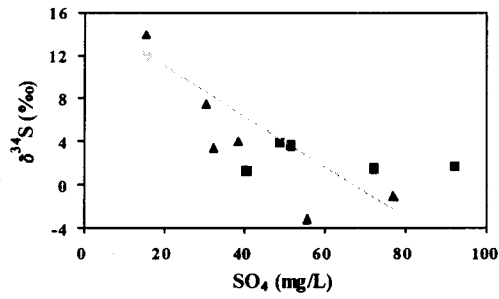


Fig. 8 Sulfate versus sulfur isotope. The arrow indicates that the reducing of sulfur.

Consequently, hydrochemical processes taking place in an alluvial aquifer of the Buyeo area could be successfully explained by some stoichiometrically balanced chemical reactions, which was also validated by thermodynamic considerations and stable isotopic data. The results of this study will be used to control pollution sources and to plan the technology for secure water supply in an alluvial setting around rivers.