The hydrochemical, isotopic, and multivariate statistical assessment of nitrate contamination of groundwater in rural areas of Korea

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Groundwater pollution in rural areas is significant in South Korea and elsewhere. Thus, better understanding of the sources and pathways of groundwater pollutants is needed for better management of rural water resources. We identified source (s) and fate of groundwater nitrate in three small watersheds of South Korea, based on the combined use of hydrochemical, dual isotopic (n=109), and statistical approaches for 165 groundwater samples.

The N and O isotopic compositions indicated that nitrate was predominantly derived from manure with minor contributions from chemical fertilizers. Solely based on isotopic measurements that were restricted to samples with sufficient nitrate concentrations, the local occurrence of soil-derived nitrate and denitrification was not clearly recognized. Therefore, we performed a multivariate classification (i.e., discriminant) analysis of isotope data together with 10 hydrochemical variables. The results indicated the presence of two nitrate sources: 1) manure-derived nitrate with minor organic/inorganic fertilizers in ca. 80% of all groundwater samples having a hydrochemical facies belonging to the Ca-Cl-SO_4 type and nitrate concentrations occasionally exceeding the Korean Drinking Water Standard (44.3 mg/L); and 2) natural soil-derived nitrate in ca. 5% of all samples, which showed a Ca-HCO_3 type with low nitrate concentrations. In addition, denitrification was identified in ca. 15% of the samples exhibiting a positive linear relationship (slope ≈ 0.5) between $\delta^{15}N$ and $\delta^{18}O$ values of nitrate concomittantly with decreasing nitrate concentrations. This study illustrates that multivariate statistical interpretation of isotopic and hydrochemical data can be helpful in precisely assessing the groundwater nitrate pollution in rural areas.

Molecular adhesion mechanisms of cell-(oxyhydr)oxide interaction

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Interfacial reactions in aqueous biogeochemical systems are often mediated by microorganisms that become directly attached to mineral and organic surfaces. Elucidation of mechanisms of microbe-mineral interactions at the molecular scale requires the use of *in situ* molecular spectroscopy. We are employing attanuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to identify the types of molecules and the nature of bonds that mediate interactions between cell surface biomolecules and mineral surface functional groups for a variety of systems of interest. Here we review our recent research on biomolecule-iron (oxyhydr)oxide interactions, with examples from adhesion of extracellular polymeric substances (EPS), bacterial cells (*Pseudomonas aeruginosa*, *Bacillus subtilis*), and pathogenic protozoa (*Cryptosporidium parvum*). Evidence for direct, inner-sphere complexation of biomolecular functional groups is discussed, and linkages are made to macro-scale cell transport phenomena.

Early adhesion processes likely involve some degree of mineral-surface conditioning film formation by free or cell-bound EPS. Data on the adsorption of EPS from the bacterial strains *Bacillus subtilis* and *Pseudomonas aeruginosa* to the α-FeOOH surface indicate that reaction of EPS with goethite favors preferential uptake of P-containing biomolecules relative to bulk C or N. Infrared spectroscopic data indicate that this organic P-selectivity derives from ligand exchange of biomolecular phosphoryl groups at goethite surface hydroxyls (i.e., ≡Fe-OP-R bonding). ATR-FTIR spectroscopic studies of live bacterial-Fe oxide systems also show the formation of ≡Fe-OP-R (s) bonds, suggesting that cell-bound phosphorylated molecules play an important role also in whole cell adhesion to unconditioned oxide surfaces.

The transport of pathogenic microbial contaminants is likewise affected by mineral-microbe bonding interaction. ATR-FTIR studies of *Cryptosporidium parvum* öocyst adhesion to α-Fe_2O_3 show that in the pH range where öocyst transport is most strongly retarded, cells are adhered to Fe oxide surfaces through inner-sphere complexation of carboxylate groups at Fe (III) metal centers.