

Effects of microbial communities on arsenic mobilization and enrichment in groundwater: Evidence from PLFA and 3D fluorescence analysis

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The phospholipid fatty acids (PLFA), as biomarkers of microbial community structures, and DOC 3D fluorescent signatures were appointed to understand the mobilization of arsenic (As) in groundwater from the Datong Basin. Groundwater samples were collected from recharge zones to discharge zones along the flow path according to redox sensitive parameters (Eh, NO₃⁻, SO₄²⁻). The results showed that As and DOC concentration increased gradually along the groundwater flow path. Correspondingly, the percentage of protein-like materials in DOC reduced whereas humic substances enhanced. In recharge zones, some aerobic bacteria served as the dominant species, such as *Thiothrix* (S-oxidizing bacteria), *Gallionella* (Fe-oxidizing bacteria), characterized by 16:1 ω 7, 16:0 and 18:1 ω 7 PLFAs. The biogeochemical processes were mainly governed by aerobic bacteria exploiting protein-like materials as electron donors to maintain metabolism together with depleting of O₂ and NO₃⁻ (electron acceptors), which restricted the reduction of As. While in discharge zones, the anaerobic microbes played a predominant role, such as *Desulfosporosinus* (SRB) and *Clostridia* (FeRB), indicated by cy17:0, cy19:0 and 18:1 ω 9 PLFAs. Furthermore, the positive linear correlation between humic substances and Fe, As suggested that high amounts of humic substances in DOC might interact and enhance the transport of As and Fe in aqueous environments. SRB and FeRB mainly utilized humic substances as energy sources for respiratory action, and simultaneously motivated biogenic reductive dissolution of Fe(III) hydr(oxides) and reduction of As(V), SO₄²⁻, resulting in geogenic immobilized As reductive desorption into aquifers. Nonetheless, the negative relationships between SRB/FeRB and As/Fe contents demonstrated that the reductate HS⁻ could react with Fe(II) and As(III) to form secondary Fe(II) sulfides or As-bearing sulfides, which subsequently sequestered As from groundwater via sorption or coprecipitation. In conclusion, As mobilization and enrichment are controlled by diverse microbial communities which catalyze multiple biogeochemical processes.