



Assessing redox process controlling C, N and S cycling in a coastal aquifer by multi-isotopic approach in south of Pearl River Delta, China

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The coastal groundwater system was investigated to assess how redox processes control C-N-S cycling in south of Pearl River Delta, China. The confined aquifers characterized by a highly reducing environment are influenced by seawater intrusion, while the unconfined aquifer under oxidizing environment is unaffected by seawater intrusion. For unconfined aquifer, the $\delta^{15}\text{N}$ values suggested ammonium and nitrate originate from manure and sewage. The $\delta^{13}\text{CDIC}$ signal suggested DIC mainly derived from soil CO_2 and weathering of carbonate rocks. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ signals of sulfate suggested SO_4^{2-} originate from the dissolution of continental evaporate. C-N-S was not influenced by reduction process in unconfined aquifer. For confined aquifer, $\delta^{15}\text{NNH}_4$ signal indicated that ammonium derived from the mineralization of organic matter. The extremely high ammonium content were mainly found in the first confined quaternary aquifer and partial fissure confined aquifer as the overlying impermeable layer (M1) contain rich organic matter. Organic matter always act as electron donor while NO_3^- , Mn(IV) , Fe(III) , SO_4^{2-} and CO_2 act as electron acceptor. Anyway, significant bacterial sulfate reduction (BSR) was observed as the positive correlation between $\delta^{34}\text{SSO}_4$ and $\delta^{18}\text{OSO}_4$ and negative correlation between SO_4^{2-} contents and $\delta^{34}\text{SSO}_4$. Extremely high CH_4 concentration suggested the existence of methanogenic bacteria (MPB). Since carbon isotope was depleted by the BSR but enriched by the methanogenesis, a wide range of $\delta^{13}\text{CDIC}$ values was found in the confined aquifers. As the intermediate products, acetate, formate and H_2 consumed by SRB and MPB were the key factors driving organic matter mineralization. It suggested the sulfate brought from seawater intrusion and CO_2 reduction urged the releasing of ammonium in the confined aquifer system. Anyway, the exhausted of sulfate in confined aquifers made CO_2 reduction become the key factor for organic matter mineralization in future. Furthermore, this study highlight the multi-isotopic method coupled with hydrochemistry data can illustrate the C-N-S cycling in the coastal groundwater system.