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Molecular characterization of dissolved organic matter in groundwater of a coastal aquifer: microbial processing of sediment sourced organics

Yan Zheng[1,2], Peng Zhang[1,2], Xuejing Wang[3], Yinghui Wang[1,2], Hailong Li[1,2], and Junjian Wang[1,2]
[1]State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China;
[2]Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China.
[3]Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China.

Interest has grown in the land-ocean continuum as an energy and material exchange hotspot between the fresh water and saline water ecosystems, including its role in global carbon cycle. Despite progress, carbon cycle especially the biogeochemistry of dissolved organic carbon (DOC) in subsurface environment across the land-ocean continuum is inadequately illustrated. Using fluorescence spectroscopy and ultra-high-resolution mass spectroscopy, this study investigated the molecular characteristics of a broad array of dissolved organic matter (DOM) molecules in shallow groundwater from a coastal aquifer of Guangdong Province. A total of 21 groundwater samples were obtained from 5 multilevel monitoring wells (W1-W5) installed to depth 1 m – 13 m along a transect located 0 m to 65 m from the coast. The infiltration rate ranged from 0.79 to 23.51 m/d, possibly reflecting a less permeable layer between ~ 9 m to ~ 12 m depth. Above this layer consisted of clay lenses, salinity (3.93‰ - 32.43‰) decreases with depth, coinciding with a linear drop of ORP value from a high of +101 mV to a low of -131.90 mV at 8 m depth. The progressively more reducing condition with depth is likely fueled by DOM released from the clay, supported by simultaneous increases of DOC (0.46–2.36 mg/L), DIC (24.62–46.71 mg/L) and DIN (0.03–2.37 mg/L) concentrations and the fluorescence index (FI) with depth. Further, except for two samples (W3-13 m and W5-8 m) with low degradation index (IDEG) of 0.47 and 0.32, of the 11190 molecular formulae of DOM identified by ultra-high-resolution mass spectroscopy molecular formulae with high relative abundance (average ~86.0%) were present in the other 19 samples (90%), indicating the existence of a core pool of DOM compounds with similar molecular compositions despite a strong redox gradient and evidence for microbial processing based on fluorescence spectroscopy data. This core pool of DOM compounds displayed high IDEG (0.82±0.06), high %lignin-like DOM (85.9±2.6), and high abundances of carboxylic-rich alicyclic molecules (%CRAM: 69.5±3.4) that are generally considered to be refractory. Therefore, consumption of labile DOM is reasoned to have taken place, resulting in the prevalence of stable DOM in saline groundwaters of coastal aquifers.

Key words: Coastal aquifers; Groundwater; Dissolved organic matter; 3D-EEMs; FT-ICR MS