Chemical Geology 487 (2018) 76–85

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Dynamic changes of dissolved organic matter during nitrate transport in a loose-pore geothermal reservoir

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ARTICLE INFO

Editor: K. Johannesson

Keywords:
Dissolved organic matter
Fluorescence
Soluble microbial products
Denitrification
Loose-pore geothermal reservoir

ABSTRACT

The dynamic changes of dissolved organic matter (DOM) during nitrate transport were investigated to explore the relationship between carbon sources and the nitrate reduction process in a loose-pore geothermal reservoir. Batch experiments were performed at four temperature levels (4 °C, 25 °C, 35 °C, and 45 °C) to determine the characteristics of the DOM extracted from the geothermal reservoir matrix. According to its fluorescence spectra, fluorescence index (FI), and biological/autochthonous index (BIX), the DOM was mainly derived by autochthonous microbial processes. Column experiments were carried out at 25 °C, 35 °C and 45 °C to determine the dynamic changes of the matrix DOM during nitrate transport in the simulated geothermal reservoir. The dynamic changes of the FIs; the fluorescence intensities (divided by dissolved organic carbon) of peaks B_1 and T_1; and concentrations of NO_3^--N, NO_2^--N, NH_4^+-N and the total dissolved inorganic nitrogen (Σ*N*) in the column effluent within 412 h (10.5 PV) indicated that the reduction rate of nitrate and the production of denitrifiers were enhanced with an increase in temperature. Although a red shift of peak T_2 during experiment at 35 and 45 °C implied the variation of the aromatic components of DOM during denitrification, low molecular weight aliphatic hydrocarbons in the matrix DOM were more active as electron donors than the aromatic compounds, as indicated by the variations of the effluent pH and $SUVA_{254}$ values. No obvious trend in the variation of the BIX with temperature was observed possibly due to the short test duration of the column experiments. The findings should advance our understanding of the biological transformation of nitrate in loose-pore geothermal reservoirs.

1. Introduction

In Kaifeng City, North China Plain, geothermal water has been exploited and utilized for drinking, bathing, medical treatments, and health care for nearly 30 years. It is of the HCO_3^--Na^+ type and is categorized as soft and alkalescent water. It is mainly extracted from aquifers buried > 600 m deep in the newly formed Minghuazhen Formation and Guantao Formation (Hall I) with a temperature above 35 °C (Yang et al., 2004; Wang and Huang, 2009). According to its burial conditions, hydraulic characteristics, and exploitation conditions, the aquifer below 600 m in Kaifeng City can be divided into eight subaquifers, with > 20 m of clay or mudstone between each subreservoir. The mean value of geothermal gradient is 3.3 °C/100 m. The quantity of geothermal water exploited from four of the subaquifers in the Minghuazhen Formation with a depth of 600–1400 m accounts for > 80% of the total volume of geothermal water utilized in the city. The geothermal water temperature for the above four subaquifers is between 35 °C and 55 °C. With the annual increase of water extraction volume, the number of geothermal water extraction wells has increased from 50 in 2004 to > 90 to date.

The overextraction of geothermal water from a loose-pore geothermal reservoir with depths between 600 and 1400 m in Kaifeng City, Henan Province, China, over the last few years has caused many hydrogeological and environmental problems, such as the drop of the water table and increased contents of NO_2^--N and NH_4^+-N in the geothermal water. As the structure of the wells are maintained in good conditions and the water pumped out of the wells is always in the normal temperature range, the shallow groundwater does not pollute the underground water down to a depth of over 600 m through the pipes (Wang et al., 2013; Zhao et al., 2014). Through column experiments, Zhao et al. (2016) did not observe any accumulation of nitrite under the simulated low-temperature geothermal conditions during the nitrification of ammonium ion. However, high levels of nitrite and ammonium were observed during the incomplete denitrification and dissimilatory

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https://doi.org/10.1016/j.chemgeo.2018.04.018
Received 4 December 2017; Received in revised form 8 April 2018; Accepted 11 April 2018
Available online 13 April 2018

nitrate reduction to ammonium (DNRA) processes at an average Darcy flux of 0.08 cm/h at temperatures of 35 °C and 55 °C in the column experiments because the types and amounts of carbon sources and bacteria were limited (Zhao et al., 2014). The phenomenon has also been observed in the geothermal water in Kaifeng City at depths between 600 and 1800 m. The efficiencies of the conversion of nitrate to nitrite and ammonium are enhanced with an increase in dissolved organic carbon (DOC), which could be used to quantify the presence of dissolved organic matter (DOM) in aquatic system (Matilainen et al., 2011; He et al., 2016). Hence, studying the mechanism of nitrate denitrification in geothermal water with low DOM content in Kaifeng City is a worthwhile endeavor.

DOM is a heterogeneous mixture of organic compounds including chemically defined compounds such as carbohydrates, proteins and humic substances (fulvic and humic acids), which originate from terrestrial or aquatic sources and from anthropogenic inputs, such as wastewater effluent (Leenheer and Stedmon, 2009). As surface water or shallow groundwater does not pollute underground water down to a depth of over 600 m through pipes (Wang et al., 2013), organic contaminants are excluded from the studied geothermal water. According to previous studies (Benedetti et al., 1996; Li et al., 2006; Saadi et al., 2006; Gondar et al., 2008; Wang et al., 2014), DOM has a wide range of ecological and geochemical functions: it binds protons, heavy metals, and organic contaminants; it serves as a source of energy for microorganisms; it facilitates light absorption, aggregation, and photochemical reactivity; and so on. Thus, the composition of DOM is spatially and temporally dependent on and associated with source material variations, environmental transformation processes, and adsorption; such relation has been intensively investigated in water, plant, and soil ecosystems (Coble, 1996; Weishaar et al., 2003; Hudson et al., 2007; He et al., 2009; Hassouna et al., 2012; Carstea et al., 2016; Tye and Lapworth, 2016). However, the temporal variations of DOM in geothermal water at depths below 600 m have not yet been reported. Although DOC has been measured in column experiments at six temperature levels (Zhao et al., 2014), no study has explored the composition and characterization of DOM derived from a studied geothermal reservoir matrix and its dynamic changes during nitrate reduction, which are highly correlated with denitrification. Therefore, efforts should be made to explore the dynamic changes of DOM during nitrate reduction in geothermal water so as to enrich our understanding of the biological transformation of nitrate. The processes related to the C cycle in underground pore water at depths below 600 m are also worth investigating.

Fluorescence spectroscopy and ultraviolet and visible (UV–Vis) absorbance spectra have been widely used in many studies to understand the source and composition of DOM in groundwater, surface water, wastewater and terrestrial ecosystems (Hudson et al., 2007; He et al., 2009; Birdwell and Engel, 2010; Korak et al., 2014; Wang et al., 2014; Carstea et al., 2016; Tye and Lapworth, 2016). A recent analysis of DOM fluorescence focused on the use of three-dimensional excitation-emission matrices (3DEEMs), which could offer various possibilities of data interpretation, including simple peak picking, fluorescence regional integration, self-organizing maps, and even the complex parallel factor analysis. Being more informative than the traditional single-scan technique, 3DEEMs have been widely developed to assess the quality of natural water, soil, raw sewage and effluents, industrial or farm discharges into natural systems, etc. Moreover, it has been recommended as a useful tool to estimate the biodegradation of DOM derived from wetland soils, wastewater and phytoplankton (Stedmon and Markager, 2005; Saadi et al., 2006; Hudson et al., 2007; Carstea et al., 2016; Fellman et al., 2010). Fluorescence-derived indices, such as the fluorescence index (FI), biological/autochthonous index (BIX), and humification index, have also been widely used to analyze the characterization of DOM. UV–Vis absorption spectroscopy measures the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. The different wavelengths ranging from 220 nm to 280 nm are believed to identify different chromophores of DOM. Despite its tendency to only represent aromatic characters, UV_{254} has been identified as a rough indicator of overall DOM concentration (Korshin et al., 2009). $SUVA_{254}$ and $SUVA_{280}$ are reported to be strongly correlated with aromaticity and molecular weight (Weishaar et al., 2003). Ratios between two different wavelengths, such as A_{250}/A_{365}, A_{254}/A_{436}, or $A_{254}/_{204}$, are also useful to describe DOM characterization, including the types of polar functional groups, molecular weight, aromaticity, etc. (Li et al., 2009; Wang et al., 2014).

The current study aims to (1) characterize DOM extracted from the studied geothermal reservoir matrix through batch experiments; (2) investigate the transport mechanism of nitrate and variations of nitrate reduction patterns under simulated low-temperature geothermal conditions through column experiments; and (3) quantify the dynamic changes of DOM through the determination of DOC, $SUVA_{254}$, FI, BIX and UV–Vis 3D fluorescence spectra during nitrate transport at temperatures of 25 °C, 35 °C, and 45 °C.

2. Materials and methods

2.1. Batch experiment methodology

The used loose-pore geothermal reservoir matrix was obtained from a geothermal reservoir comprising the Minghuazhen Formation from the Neogene Period with a depth between 600 and 1400 m and bared from a 60 m-deep valley in Wang-Gou Village, Qu-Liang Town, Xin-Mi County, China (Wang et al., 2013). Before use, all samples were air dried and ground to pass through a 2 mm screen. The total organic carbon (TOC) and total nitrogen of the matrix were 0.0745% and 0.0093% (Zhao et al., 2011), respectively.

As the carbon sources released from the studied matrix were the major electron donors that could contribute to the nitrate denitrification in the studied geothermal water, we first investigated the characterization of the matrix DOM before exploring the dynamic changes of DOM during nitrate transport in the loose-pore geothermal reservoir. Thus, batch studies were conducted first in a temperature-controlled shaker using 150 mL deionized water with 30.0 g of the loose-pore geothermal reservoir matrix. The agitation speed of the shaker was fixed at 150 rpm for all batch experiments. The samples collected at different time intervals (0.25, 0.5, 1, 2, 4, 6, 12, and 24 h)were centrifuged at 12,000 rpm at 4 °C for 20 min. The experiments were carried out individually at four temperature levels ranging from 4 °C to 45 °C. The obtained supernatant was filtered through a 0.45 μm filter membrane and then kept at 4 °C in the dark before the measurement of UV–Vis absorbance, 3D fluorescence spectra, pH, and electrical conductivity (EC) within 24 h.

2.2. Column design

Two identical acrylic columns (with a diameter and height of 11 and 90 cm, respectively) were prepared for the hand packing of the loose-pore geothermal reservoir matrix used in the batch experiments. The structure of the column, the method of packing the air-dried matrix, and the column setups placed in the dark inside an incubator were the same as those used in our previous study (Zhao et al., 2014). The average porosity value of the packed matrix was 0.35. Although the nitrate breakthrough curves (BTCs) at three Darcy fluxes ranging from 1.23 cm/h to 3.67 cm/h at 35 °C were studied (Zhao et al., 2014), the dynamic changes of carbon sources in the experiments which are vital to the denitrification process were not investigate. Thus, nitrate elution experiments were carried out in the current work at a Darcy flux of 0.8 cm/h for 10.5 pore volume (PV)of column effluents (about 412 h) at temperatures of 25 °C, 35 °C, and 45 °C to explore the dynamic changes of DOM released from the packed matrix during nitrate transport. At the end of each experiment, the porous medium in the column was leached for at least 7 days with deionized water to remove residual