



Production of hydroxyl radicals from Fe(II) oxygenation induced by groundwater table fluctuations in a sand column



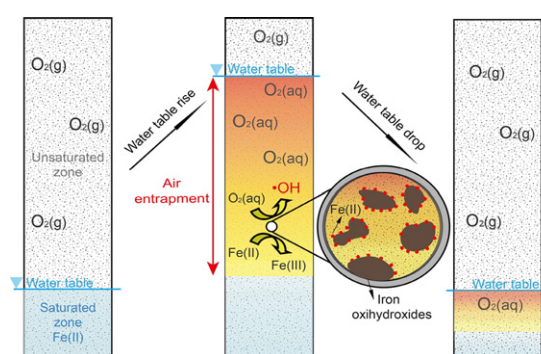
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HIGHLIGHTS

- Groundwater table fluctuations induce ferrous iron oxygenation.
- Hydroxyl radicals could be produced during groundwater table fluctuations.
- Hydroxyl radicals are supposed to produce from oxygenating adsorbed Fe(II).
- Hydroxyl radicals potentially contribute to abiotic transformation of substances.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural and artificial processes often cause the fluctuation of groundwater table, inducing the interaction of O₂ from the unsaturated zone with reduced components such as Fe(II) from the saturated zone. In light of previous findings that hydroxyl radicals (\bullet OH) can be produced from Fe(II) oxygenation, we hypothesize that \bullet OH could be produced during groundwater table fluctuations. Therefore, this study aims to measure the production of \bullet OH during water table fluctuations in a simulated sand column. Deoxygenated water in the absence and presence of 20 mg/L Fe²⁺ (pH 6.5) was fed into the sand column. Water table fluctuations were manipulated to observe O₂ entrapment, Fe²⁺ oxygenation and \bullet OH production. Results showed that O₂ in the pore air was efficiently entrapped by the rise of water table at the tested rates of 0.16–0.34 cm/min (or 0.10–0.20 m/h), and the dissolution of entrapped O₂ into the pore water led to the oxygenation of Fe²⁺. Production of \bullet OH was presumably attributed to oxygenation of the Fe²⁺ adsorbed on Fe(III) oxyhydroxides generated *in situ*. In a total of 4 cycles of fluctuations, the cumulative \bullet OH at all the elevations increased progressively, attaining 2.7 μ M in the zone near the water table in the 4th cycle. We suggest that \bullet OH produced from water table fluctuations could induce an overlooked pathway for contaminant transformation in the fluctuation zone.

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1. Introduction

Groundwater table and the associated capillary fringe is a transition zone between the unsaturated and saturated zones in shallow subsurface environments. Groundwater table often fluctuates due to natural

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processes like seasonal raining and drying, interaction of groundwater and surface water and tidal processes (Duan et al., 2015; Hsieh et al., 2015; Sawyer et al., 2014). The fluctuation can be also caused by human activities such as groundwater extraction for drinking and irrigation, water conservation projects and artificial groundwater recharge (Datry et al., 2004; Deng et al., 2016; Su et al., 2014). The redox potential in a vertical profile generally decreases from oxidizing in the unsaturated zone to reducing in the saturated zone under static conditions, but varies in response to groundwater table fluctuations (Duan et al., 2015; Malard and Hervant, 1999; Rezaeezhad et al., 2014; Sawyer et al., 2014). An increase in groundwater table carries the O₂-defective pore water upwards to entrap the soil pore air (Fry et al., 1997; Haberer et al., 2011); in contrast, a decrease in groundwater table leads to the exposure of sediments previously saturated to the pore air (Farnsworth et al., 2012; Sinke et al., 1998). As a consequence, the redox condition in the zone suffering from groundwater table fluctuations varies between reducing and oxidizing.

There have been a lot of investigations about the natural attenuation of contaminants induced by groundwater table fluctuations (Dobson et al., 2007; Farnsworth et al., 2012; Fry et al., 1997; Gilson et al., 2015; Holman et al., 1999; Lee et al., 2001; Reddi et al., 1998; Sinke et al., 1998). Biological transformation is normally deemed as the predominant mechanism for contaminant attenuation in the fluctuation zone (Dobson et al., 2007; Farnsworth et al., 2012; Fry et al., 1997; Holman et al., 1999; Lee et al., 2001; Reddi et al., 1998; Sinke et al., 1998). For example, the electron acceptors such as O₂ entrapped by the rise of the groundwater table were believed to biodegrade petroleum hydrocarbons in the fluctuation zone (Dobson et al., 2007; Lee et al., 2001; Reddi et al., 1998). Entrapped O₂ was also proven to induce biological oxidation of Mn(II) (Farnsworth et al., 2012) and mineralization of polycyclic aromatic hydrocarbons (Holman et al., 1999). However, the abiotic mechanisms for contaminant attenuation are largely overlooked in the groundwater table fluctuation zone.

During the fluctuation of groundwater table, O₂ from the pore air is entrapped and dissolved into the pore water, triggering the chemical and biological reactions of dissolved O₂ (DO) with reduced components such as Fe(II) and organic carbon. It is substantiated that the reactions of O₂ with Fe(II) can produce reactive oxygen species (ROS) (Melton et al., 2014; Rose and Waite, 2002), particularly the strongly oxidizing hydroxyl radicals (•OH) (Page et al., 2013; Minella et al., 2015; Tong et al., 2016; Zhang et al., 2016), and the •OH produced can induce the oxidative transformation of environmental contaminants (Ai et al., 2013; Tong et al., 2016; Yan et al., 2016; Zhang et al., 2016; Zhu et al., 2017). For example, Ai et al. (2013) found that Fe(II) coated on zerovalent iron surface can activate O₂ to produce superoxide and •OH, leading to the oxidation of 4-chlorophenol; Yan et al. (2016) noted the oxidative transformation of enrofloxacin by the •OH produced by oxygenation of biologically reduced hematite; and our group recently highlighted the production of •OH upon oxygenation of reduced Fe(II) minerals from field sediments (Tong et al., 2016), mackinawite (Cheng et al., 2016), pyrite (Zhang et al., 2016) and simulated acid mine drainage (Zhu et al., 2017). As a consequence, it is reasonable to speculate that •OH could be produced from the interactions of O₂ from the pore air with reduced Fe(II) from the pore water and sediments caused by groundwater table fluctuations.

Therefore, this study aims to check the hypothesis of •OH production during groundwater table fluctuations. To achieve this goal, the water table in a sand column was manipulated in the lab so that it fluctuated periodically. Efficiency of O₂ entrapment from the pore air into the pore water was firstly examined using Fe²⁺-free deoxygenated water. Then, O₂ entrapment, Fe²⁺ oxidation and •OH production were investigated by feeding Fe²⁺-containing deoxygenated water. For the measurement of •OH produced, sodium benzoate (BA) was added to quantitatively trap the •OH because of the quick reaction ($k_{\text{BA}\cdot\text{OH}} = 5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Buxton et al., 1988).

2. Materials and method

2.1. Chemicals

BA (99.5%), *p*-hydroxybenzoic acid (*p*-HBA, 99%) and ferrous sulfate (99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-(*N*-morpholino)ethanesulfonic acid (MES, 99%, Biosharp Corporation, China) was used as the pH buffer in the presence of Fe²⁺. Deionized (DI) water (18.2 MΩ·cm) was obtained from a Heal Force NW ultrapure water system. All the other chemicals used in the experiments were above analytical grade.

2.2. Experimental setup

The experimental setup used for groundwater table fluctuations was designed referring to Farnsworth et al. (2012). A schematic diagram is shown in Fig. 1. A vertical acrylic column (13 cm inner diameter × 34 cm length, termed “sand column”) was used to observe water table fluctuations. A perforated plate was placed at a distance of 5 cm from the bottom for water distribution. Both the bottom and top of the sand column were attached with removable acrylic plates, which were fixed to the flanges with screws and sealed with rubber O-rings between the plates and flanges. One hole was drilled in the bottom plate to allow for the gas and water flow, and another hole was drilled in the top plate to balance the pressure. In one side of the sand column, 5 DO probes (JPB-607A, Shanghai INESA) were inserted horizontally at a distance of 5 cm for *in situ* monitoring the DO concentration. The locations of the 5 probes were sequentially 7, 12, 17, 22 and 27 cm from the bottom. In the opposite side at the same depths, 5 ports with Teflon septa inside were drilled for sampling the pore solutions through a syringe. A vertical acrylic column (10 cm inner diameter × 56 cm length, termed “feed column”) filled with deoxygenated solutions was used to control the fluctuation events. Three holes were drilled in the top, with one for injecting solution and the other two for purging N₂. The deoxygenated solutions from the feed column were pumped upward into the sand column by a peristaltic pump (Luxi, model HL-2, China).

2.3. Experimental procedure

At the beginning of experiments, the sand column was attached to the bottom plate, and the 5 DO probes were installed. Then, about 5 kg of sand (0.425 mm in size, Sinopharm Chemical Reagent Co., Ltd., China) was packed into the sand column. Our measurements showed that Fe²⁺ leached from the sand (1 M HCl) was below the detection limit. Manual compaction was applied every 5 cm depth during the packing, giving the porosity of 0.41. It is notable that the sand was replaced only for the experiments involving Fe²⁺ oxygenation. After packing the column, the top plate was covered, leaving the hole open to air. High-purity N₂ (99.999%) was introduced into the column from the bottom hole to purge O₂ in the sand column. It was found that the DO probes were sensitive to O₂ content in the pore gas. Thus, the data shown in the probe was used as an indicator of O₂ in the pore gas under unsaturated conditions. After 60 min purging, all the DO values were below 0.1 mg/L. Then, the hole in the bottom plate was switched to the feed column, from which the aqueous solution was pumped into the sand column. About 3.5 L of deoxygenated solution were filled in the feed column which was purged by N₂ for 60 min and then connected to a collapsing gas bag filled with N₂. The DO concentration in the feed column was measured to be less than 0.1 mg/L.

A total of 4 sets of experiments were carried out. The main operation parameters are displayed in Table 1. The first set (no. C1) aimed to observe the entrapment of O₂ from the pore air into the pore water during cycles of water table fluctuations. Deoxygenated DI water from the feed column was pumped into the sand column at a constant flow of 0.38 cm/min (or 50 mL/min). The water level in the sand column was

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