Geoderma 325 (2018) 141–151

Contents lists available at ScienceDirect

Geoderma

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

# Wetland saturation with introduced Fe(III) reduces total carbon emissions and promotes the sequestration of DOC

Yuanchun Zou[a], Sijiang Zhang[a,d], Lili Huo[b], Guangzhi Sun[c], Xianguo Lu[a], Ming Jiang[a], Xiaofei Yu[a,*]

[a] Key Laboratory of Wetland Ecology and Environment & Jilin Provincial Joint Key Laboratory of Changbai Mountain Wetland and Ecology, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China
[b] Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, China
[c] School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia
[d] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Handling Editor: David Laird

*Keywords:*
Fe redox cycling
Organic carbon decomposition
Soil-free incubation
$CO_2$:$CH_4$ ratio
Depressional wetland
Agricultural drainage

ABSTRACT

Solutions containing dissolved organic carbon (DOC) from a depressional wetland that receives agricultural drainage water were incubated in pure quartz sands with $FeCl_3$ added as the main electron acceptor. The effects of three factors (the water, DOC, and Fe contents) on the $CO_2$ and $CH_4$ production rates, integrated cumulative C emissions and Fe-OC co-precipitation were studied. The results showed that $CO_2$ production during the DOC mineralization process was facilitated by Fe(III) reduction at the expense of $CH_4$ production. Additionally, the cumulative $CO_2$ emissions determined by integrating the temporal curves of $CO_2$ production were negatively correlated with those of $CH_4$ ($r = -0.48$, $p < 0.01$). Extremely large ratios of the $CO_2$:$CH_4$ production rate (13,762 and 44,885 under two soil water conditions: saturation and flood conditions of twice the saturation level) were observed. These ratios were likely caused by simultaneous anaerobic fermentation, microbial respiration, and methanogenesis suppression triggered by iron reduction. The effects of exogenous Fe(III) inputs on total C emissions (as the sum of integrated cumulative $CO_2$ and $CH_4$) were only dependent on soil water conditions during the initial period of the experiment, and flooded conditions increased total C emissions by as much as double. Increased ratios of Fe inputs to C contents were found to proportionally increase the total C emissions ($R^2 = 0.32$, $p < 0.01$). Under saturated conditions, the co-precipitation of Fe-OC complexes prevented the remainder of the DOC from undergoing mineralization. In terms of DOC, we concluded that wetland saturation with introduced Fe(III) can reduce total C emissions from anaerobic respiration and promote C sequestration.

## 1. Introduction

The microbial decomposition of organic carbon, known as carbon (C) mineralization, is one of the key processes in natural biogeochemical C cycling. C mineralization can be caused by either aerobic or anaerobic respiration, when gaseous $CO_2$ and $CH_4$ are emitted (Lovley, 1987). The mineralization of soil organic matter is critical for the global C budget because of the enormous organic C stock in the pedosphere (Davidson and Janssens, 2006), especially in peatland ecosystems (Gorham, 1991; Blodau, 2002).

The mineralization rate is controlled by the internal characteristics of organic C (OC) and external environmental factors (Blodau, 2002). Schmidt et al. (2011) suggested that the persistence of soil OC (SOC) is primarily influenced by non-molecular characteristics, such as ecosystem characteristics, and that the stability of SOC is not only controlled by its molecular structure but also by environmental and biological factors. Hence, major external environmental factors (such as temperature, moisture, wet-dry cycles, and microbial and enzymatic activity) should be comprehensively considered (Chow et al., 2006; Hassan et al., 2015). These interactive effects are complicated and sometimes conflicting according to various laboratory and field analyses. This complex regime may be partially attributed to the effects of terminal electron acceptors (TEAs) on $CO_2$ and $CH_4$ emissions.

Based on thermodynamic theory and the balance of chemicals, any mineralization of OC to $CO_2$ is influenced by the electron transfer coupled with the redox transformation of other elements. In organic-rich wetland soils or sediments, OC decomposition is generally limited due to the lack of TEAs (Song et al., 2015). The preferred TEAs are

* Corresponding author at: Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, China.
*E-mail address:* yuxf@iga.ac.cn (X. Yu).

https://doi.org/10.1016/j.geoderma.2018.03.031
Received 28 December 2017; Received in revised form 14 March 2018; Accepted 24 March 2018
Available online 06 April 2018

(sequentially from strong to weak) $O_2$, $NO_3^-$, Mn(IV), Fe(III), $SO_4^{2-}$, and $CO_2$ as the energy generated decreases (Reddy and Delaune, 2008). Among these TEAs, the process of Fe(III) reduction has been well discussed (Lovley, 1987; Roden and Wetzel, 2002; Davidson and Janssens, 2006; Küsel et al., 2008; Hanke et al., 2013). Notably, the microbial reduction of Fe(III) is one of the most important mechanisms of anaerobic OC decomposition in wetland soils and sediments, and it affects C emissions, nutrient cycling, organic pollutant degradation, heavy metal transfer, etc.

Fe(III) reduction has been confirmed to account for a major proportion of $CO_2$ emissions via anaerobic respiration, and it considerably decreases $CH_4$ emissions via competitive inhibition or Fe toxicity to methanogens in wetland soils and sediments (Bodegom et al., 2004; Reiche et al., 2008; Lipson et al., 2010; Chen et al., 2014; Karvinen et al., 2015). These effects are influenced by Fe enrichment, either through dissolved Fe transporting from surface water or capillary effects from groundwater, and then Fe oxidation can occur through the aeration of the root systems of vascular wetland plants (Weiss et al., 2003; Dettling et al., 2015).

As a reactive fraction of SOC and the key link between solid plant/microbial organic C and gaseous $CO_2$ and $CH_4$, dissolved organic C (DOC) is a sensitive component during C cycling and very important in numerous soil processes, including SOC mineralization (Kalbitz et al., 2000; Chow et al., 2006; Preston et al., 2011) and retention (Sodano et al., 2017). High concentrations of low molecular weight labile DOC are generally present in wetland soils and provide substrates for microbes. A portion of labile DOC can have a large electron accepting and donating capacity and play a significantly role in anaerobic respiration (Lovley et al., 1996). Therefore, the addition of DOC can simultaneously enhance $CO_2$ and $CH_4$ emissions under anaerobic conditions (Dubinsky and Firestone, 2010; Peng et al., 2015). Compared with the numerous studies of SOC mineralization and Fe(III) reduction, few studies have focused on the relationship between DOC mineralization and Fe(III) reduction. Both positive and negative correlations have been observed between DOC and Fe concentrations (Hall and Silver, 2013; Hanke et al., 2013), and these differences can be attributed to the different reactions involving solid OC and liquid DOC under different hydrogeochemical conditions (Chow et al., 2006).

Under normal circumstances, the supply of Fe(III) is limited in wetland soils (Dettling et al., 2015). Fe redox cycling in these soils has received little attention because Fe concentrations are often too small to contribute to C mineralization (Blodau, 2002), despite the importance of Fe in the other ecosystems (Azam and Finneran, 2013; Hall and Silver, 2013). The depressional wetlands in the Sanjiang Plain Wetland system, however, are special for they partially supplied with surface runoff except precipitation. Drainage ditch networks separate the surviving natural wetlands from each other. Therefore, it is possible that nutrients from agricultural drainage are transported from croplands to downstream wetlands. The waterborne transport of Fe through lateral subsurface flow or surface runoff, both from natural wetlands and irrigated farmlands, has been documented (Zou et al., 2011). Consequently, the OC mineralization and C emissions in these depressional wetlands have changed as a result of anthropogenic Fe inputs. Although there are vast wetlands affected by exogenous Fe introduction, the effects of Fe(III) reduction on C emissions have not been studied before in these wetlands, despite their importance in the regional C balance and global climate warming.

In this study, an in vitro experiment involving the soil-free incubation of DOC solutions extracted from an isolated depressional wetland in the Sanjiang Plain is performed with $FeCl_3$ added as the main electron acceptor. The objectives of this study were (1) to analyze the interactive effects of the hydrological regime, DOC and TEA supplies on the mineralization of DOC and (2) to assess C emissions when Fe-containing agricultural drainage is introduced for wetland water replenishment.

## 2. Methods

### 2.1. Experimental device

To avoid the introduction of an extra C source from soil organic matter or the microbial or plant biomass, the incubation medium in this experiment was analytically pure quartz sand (0.30–0.71 mm particle size, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The quartz sand was washed with diluted hydrochloric acid (2 mol $L^{-1}$) for 24 h and repeatedly rinsed with deionized water until the filtrate became pH neutral. Then, the samples were heated to 600 °C to remove the residual Fe and C before incubation. Next, 500 mL glass jars with rubber septa were used for the incubation. A three-way valve was plugged into the septa to control the exchange of air. A plastic gas syringe (50 mL) with a three-way stopcock, which could be connected to a three-way valve, was used to collect the gas produced in each jar during the incubation.

### 2.2. Experimental design

The experiment was designed considering three factors: water × Fe × DOC. The amount of water was increased to saturation without excess overlying water (110 g of quartz sand mixed with 40 mL of solution), and flooded conditions were also investigated (free overlying water was present; the same amount of sand with 80 mL of solution). Additionally, three levels of both Fe and DOC were established. The two hydrologic conditions, saturation and flooding, were selected to simulate the water replenishment options for a local wetland and to test the responses of OC mineralization under different levels of $O_2$ availability. Controls were also created, for which only 40 or 80 mL of deionized water was added to the jars. The difference in the air content between the solutions was non-significant. All treatments and controls had three replicates. The total number of incubation jars was 60, including 54 treatments (2 water × 3 Fe × 3 DOC × 3 replicates) and 6 controls (2 water × 3 replicates).

According to a survey from a previous project, the average TFe and DOC concentrations in the top soil layers of the typical natural wetlands in the Sanjiang Plain are 0.32 and 22.4 mg $L^{-1}$, respectively, and the average TFe content in the ditch that receives farmland drainage water near the wetlands is 2.23 mg $L^{-1}$. Consequently, the three Fe treatments were set at 0.32 mg $L^{-1}$ (LFe, the mean content in the top layer of natural wetland soils), 1.115 mg $L^{-1}$ (MFe, half of the concentration in agricultural drainage water) and 2.23 mg $L^{-1}$ (HFe, the mean content of farmland drainage water) using chemically pure $FeCl_3{\cdot}6H_2O$. To neutralize the acidity created by the introduction of $FeCl_3{\cdot}6H_2O$ and minimize pH variations, diluted NaOH was added. The three DOC loads were set at 22.4 mg $L^{-1}$ (low, LDOC), 44.8 mg $L^{-1}$ (medium, MDOC; two times the background content) and 89.6 mg $L^{-1}$ (high, HDOC; four times the background to stimulate extreme conditions). The DOC bulk solution was extracted from the top soil layer (0–10 cm) of a *Carex lasiocarpa* wetland on the Sanjiang Plain. The soil layer was composed of semi-decomposed organic matter and non-decomposed litter, with a dark brown color and flexible texture (Zou et al., 2009). The soil sample was extracted with deionized water, magnetically stirred for 30 min and centrifuged (3000 rpm) for 5 min. A small part of the supernatant (approximately 100 mL) that included microorganisms was stored for inoculation. The remainder of the sample was filtrated using a 0.45 μm membrane and kept as the bulk solution for DOC concentration adjustment. Because there was some $SO_4^{2-}$ (> 2 mg $L^{-1}$) in the bulk solution (Hao et al., 2004), $BaCl_2$ was used to remove the $SO_4^{2-}$. The concentrations of DOC, $SO_4^{2-}$, $NO_3^-$, Mn(IV), Fe(III) and Fe(II), as well as the pH after the pretreatment, were measured before incubation. Although the composition of DOC was not determined, the main constituents were assumed to be humic substances (Riedel et al., 2012; He et al., 2015).

An aliquot of the original DOC solution (1 mL) was added to all the