



# Concentration dynamics and biodegradability of dissolved organic matter in wetland soils subjected to experimental warming



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## HIGHLIGHTS

- Stimulatory effect of elevated temperature on DOM release was short-lived.
- Experimental warming increased DOM humicity and thus decreased its biodegradability.
- Substrate limitation due to decreased DOM biodegradability may alleviate C loss.
- Different soil types with organic contents had distinct fluorescence fingerprints.
- Integrated fluorescence indices were suitable for determining DOM character.

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## ABSTRACT

Dissolved organic matter (DOM) is the most bioavailable soil organic pool. Understanding how DOM responds to elevated temperature is important for forecasting soil carbon (C) dynamics under climate warming. Here a 4.5-year field microcosm experiment was carried out to examine temporal DOM concentration dynamics in soil pore-water from six different subtropical wetlands. Results are compared between control (ambient temperature) and warmed (+5 °C) treatments. UV–visible and fluorescence spectroscopy was performed to reveal DOM structural complexity at the end of the warming incubation. Elevated temperature resulted in initially (1 to 2.5 years) high pore-water DOM concentrations in warmed samples. These effects gradually diminished over longer time periods. Of the spectral indices, specific UV absorbance at 280 nm and humification index were significantly higher, while the signal intensity ratio of the fulvic-like to humic-like fluorescence peak was lower in warmed samples, compared to the control. Fluorescence regional integration analysis further suggested that warming enhanced the contribution of humic-like substances to DOM composition for all tested wetlands. These spectral fingerprints implied a declined fraction of readily available substrates in DOM allocated to microbial utilization in response to 4.5 years of warming. As a negative feedback, decreased DOM biodegradability may have the potential to counteract initial DOM increases and alleviate C loss in water-saturated wetland soils.

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## 1. Introduction

Dissolved organic matter (DOM) is a heterogeneous mixture of organic compounds ranging from simple, short-chain molecules to complex fulvic and humic substances leached from soils (Stutter et al., 2007). Though it only represents a small proportion of total soil organic matter in both terrestrial and aquatic ecosystems, DOM links various ecological compartments including soils to water bodies, serves as a crucial indicator of biogeochemical responses to disturbance, and provides carbon (C) and energy for microbial metabolism (Bolan et al., 2011; Kalbitz et al., 2000; Wilson and Xenopoulos, 2009). The average global surface temperature has increased by 0.74 °C since

1850 and is likely to increase by another 1.1–6.4 °C by the end of this century (Solomon et al., 2007). Wetlands are globally important carbon stores, and many are thought to be highly sensitive to climate change (Erwin, 2009) but we know little about DOM concentration dynamics and the nature of change in DOM properties under warming for a range of wetland types including subtropical wetlands.

Rising temperatures accelerate the microbial decomposition rates of soil organic matter. It is unclear for many wetland systems whether accelerated C loss associated with warming is a transitory phenomenon with almost unchanged soil organic matter contents or whether it is persistent with a net of loss of C from the soil store which is released as CO<sub>2</sub> to the atmosphere (Bengtson and Bengtsson, 2007; Kirschbaum, 2004). Data from long-term field warming incubations for mid-latitude hardwood forest soils and tall grass prairie soils have demonstrated that the stimulatory effect of rising temperature on increased CO<sub>2</sub> emission rates evident in first few years of warming was reduced so that CO<sub>2</sub>

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dropped back to similar rates to those before the elevated temperature (Luo et al., 2001; Melillo et al., 2002). The reason for long-term reductions in CO<sub>2</sub> emission from soils (after an initial emission increase) was thought to be due to the depletion of available substrate (Kirschbaum, 2004) indicating that substrate utilization by microbes is a key mechanism. Better understanding of such processes will aid predictions of soil C cycling dynamics under climate change.

The microbial utilization of DOM is controlled by its bioavailability and biodegradability, both of which strongly influence the fate of soil C stocks through influencing microbial feeding and functional physiology (Marschner and Kalbitz, 2003). Increased temperature favors desorption of high-affinity compounds binding to minerals and release of occluded organic matter from soil aggregates (Conant et al., 2011) which enhance pore-water DOM concentrations and thus the substrate bioavailability. In field studies, multiple factors simultaneously affect DOM concentrations (Stutter et al., 2007), leading to the DOM pool varying with season (Stutter et al., 2007) and soil type (Kalbitz et al., 2000). It is still unclear whether increased pore-water DOM concentrations will persist under more sustained field warming (rather than in short-term laboratory studies), given the microbially-mediated decomposition of soil organic matter and the variable levels of stability between different soil organic fractions (von Lutzow and Kogel-Knabner, 2009).

Understanding DOM utilization by microbes is limited if we ignore its chemical character related to substrate biodegradability (Kujawinski, 2011). The biodegradability of DOM is strongly affected by its structural complexity (Fellman et al., 2008). The fractions such as low molecular weight monomers with lower aromaticity and less condensed structure can be directly assimilated by microbes, while high molecular weight compounds need to be first broken down, or depolymerized to obtain energy contained within (Marschner and Kalbitz, 2003). As a result, low DOM biodegradability constrains substrate utilization and further influences C uptake, retention and export (Battin et al., 2008) even without changed DOM concentrations. There has been some DOM characterization work in peatlands subjected to degradation and restoration (Glatzel et al., 2003) which has shown that DOM composition affects CO<sub>2</sub> efflux from peatlands and that DOM composition is also driven by respiration and CO<sub>2</sub> efflux. “Studies of seasonal dynamics in DOM by Huang and Cheng (2009) suggested that higher temperature in summer and fall could lead to higher values in fluorescence spectrum intensities of chromophoric DOM compared to those in winter and early spring. So far, information about DOM chemical character in the pore-water of wetland soils under sustained warming is extremely limited, which impairs our understanding of likely wetland soil C cycling in the future.

As a highly-sensitive tool, fluorescence spectroscopy allows identification of different compounds in DOM belonging to specific regions, and helps evaluate the humicity of water samples (Chen et al., 2003; Fellman et al., 2010). Strong signal intensities of protein-like and soluble microbial byproduct-like fluorescence would suggest that the DOM contains a large hydrophilic fraction of relatively high biodegradability. Enriched aromatic and hydrophobic structures in DOM related to terrestrial-derived humic-like fluorescence indicate an increase in water humicity. These signatures combined with informative spectral indices from integrated UV–visible absorbance and fluorescence measurements provide a basis for estimating DOM biodegradability (Wilson and Xenopoulos, 2009).

In this study, a real-time temperature controlled incubation system (Zhang et al., 2012) was developed outdoors in May 2008 simulating warming scenarios to investigate the dynamics of soil pore-water DOM concentration and its chemical character over 4.5-years of incubation. UV–visible and fluorescence spectroscopy were used to distinguish different classes of DOM character. Six subtropical wetlands covering a broad gradient of soil organic matter contents (14.6 to 114 g kg<sup>-1</sup> dry soil, Table 1) were selected, given the potentially high variability of pore-water DOM concentrations in wetlands. The objectives of this

study were to: (i) test whether DOM concentrations were persistently higher in warmed samples compared to the control during 4.5-years of experimental warming; (ii) test whether warming induced changes in DOM chemical character after 4.5-years of incubations; (iii) test whether there were distinct differences in DOM response to warming between wetland soil types and (iv) to investigate why any changes in DOM occurred.

## 2. Material and methods

### 2.1. Microcosm configuration and sample description

A custom-built novel microcosm was used to simulate climate warming (Zhang et al., 2012). The microcosm involved samples being kept at current ambient temperature conditions (control) and simulated warming conditions which were continuously 5 °C above ambient temperature (warmed). The annual average temperature for samples under control is around 31 °C in the summer and around 5 °C in the winter. Specifics regarding the configuration and corresponding operation of this microcosm system have been reported previously (Zhang et al., 2012). The microcosm maintained hydrological characteristics and a humid habitat for microbial growth, offering a high resolution temperature comparison, good repeatability, and the capability to simulate warming conditions with temperature of both the control and the warmed treatments ‘naturally’ varying on a daily and seasonal basis. Each intact wetland soil core (20 cm in depth) was collected using a stainless steel column sampler, and then transferred into a transparent PVC wetland column. After that, each column was filled with corresponding overlying water (20 cm in depth) and was put into microcosm system. The microcosm system started running in May 2008 and has been in continuous operation since then. In the summer of each year when water evaporation from columns was too severe, the equal amount of mineral water was carefully added into each column about 2–3 times of the whole year. The details for preparing the wetland columns (with 6 replicates for each wetland site) were described previously (Zhang et al., 2012).

Samples were taken from study sites located in the southern region of the Taihu Lake Basin within the delta of the Yangtze River, in China. Six wetlands, with shallow water bodies of 0.8–1.5 m in depth, differing in land use and nutrient status were selected (Table 1). In brief, YaTang riverine (YT) wetland is a polluted duck farm, while XiaZhuhu (XZ) wetland is threatened by high risk of eutrophication due to intensive aquaculture and anthropogenic nutrient inputs. The soils in YT and XZ have significantly higher organic matter, nutrient (i.e., phosphorus and nitrogen) and water contents compared to others (Table 1). The wetlands named as BaoYang (BY), XiXi (XX), JinHu (JH), and Shijiu (SJ) are generally preserved for tourism and used as water reservoirs, typical of recovered wetlands. SJ was formerly a paddy field with the lowest organic matter among the six studied wetlands.

### 2.2. Non-destructive sampling for water chemical analysis

For soil pore-water sampling, a soil solution sampler (0.5 μm porous polyacrylonitrile hollow fiber, Chinese Academy of Sciences, Nanjing) described by Song et al. (2003) was horizontally embedded into the soil in each column at a fixed depth of 5 cm. About 30 mL of pore-water was sampled from each wetland column on seven occasions (both winter and summer) between July 2009 and December 2012 inclusive during 55 months of incubations, and was analyzed immediately for DOM concentrations after each sampling. At the end of the incubation (December, 2012), the sampled pore-water was also used for UV–visible and fluorescence spectral analysis. All of the following measurements were conducted after filtration of pore-water through a 0.45 μm filter.

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