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# Characteristics of dissolved organic matter following 20 years of peatland restoration

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ABSTRACT

The changes in the amounts and composition of dissolved organic matter (DOM) following long-term peat restoration are unknown, although this fraction of soil organic matter affects many processes in such ecosystems. We addressed this lack of knowledge by investigating a peatland in south-west Germany that was partly rewetted 20 years ago. A successfully restored site and a moderately drained site were compared, where the mean groundwater levels were close to the soil surface and around 30 cm below surface, respectively. The concentrations of dissolved organic carbon (DOC) at 4 depths were measured over one year. The specific absorbance was measured at 280 nm and the fluorescence spectra were used to describe the aromaticity and complexity of DOM.

The investigations showed that 20 years of peatland restoration was able to create typical peatland conditions. The rewetted site had significantly lower DOC concentrations at different depths compared to the drained site. The specific UV absorbance showed that the rewetted site had a lower level of aromatic DOM structures. The decreasing specific UV absorbance might indicate an increasing contribution of small organic molecules to DOM. It was hypothesized that the decreasing DOC concentrations and the relative enrichment of small, readily degradable organic molecules, reflect the slower decomposition of organic matter after the re-establishment of the water table. Seasonal trends provided substantial evidence for our hypothesis that reduced DOC concentrations were caused by reduced peat decomposition. During summer, the elevated DOC values were accompanied by an increase in DOM aromaticity and complexity. Our results demonstrated a close link between C mineralization and DOC production. We concluded that long-term peatland restoration in the form of the successful re-establishment of the water table might result in reduced peat decomposition and lower DOC concentrations. The restoration of peatlands seems to have a positive impact on C sequestration.



## 1. Introduction

During the last few decades, land use has changed dramatically across the globe (Lambin and Geist, 2006). These changes disturb the ecosystems and are generally accompanied by the quick loss of carbon (C) (Körner, 2003). Usually, the carbon reaches the atmosphere either directly as carbon dioxide ($CO_2$) or indirectly as dissolved organic matter (DOM). In the light of climate change, care should be taken to avoid such C losses. Nevertheless, land use change remains the second most important source of anthropogenic $CO_2$ (IPCC, 2007).

Soils are the largest terrestrial C pools (IPCC, 2007) and recover extremely slowly after disturbances have occurred. Therefore, soil C cycling is the key to developing efficient mitigation strategies of land use-induced C losses (Dawson and Smith, 2007).

In this context, peatlands are key ecosystems; they represent the largest pool of the terrestrial organic C (Gorham, 1991). Pristine peatlands are sinks for atmospheric C because decomposition is slowed down as a result of the prolonged absence of oxygen (Freeman et al., 2001). However, human activities have led to profound effects on peatland biogeochemistry, vegetation and C losses (van Seters and Prince, 2002; Strack et al., 2008; Limpens et al., 2008; Waldron et al., 2008). However, it has been demonstrated that the restoration of peatlands, which is presently typically motivated by nature conservation concerns (Pfadenhauer and Klötzli, 1996; Cooper and MacDonald, 2000), can also be beneficial (with respect to the economic aspects of

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the Kyoto Protocol) in terms of C sequestration and greenhouse gas (GHG) dynamics (Wilson et al., 2007, 2008).

The effect that rewetting of peatlands has on DOM has received little attention so far, despite the fact that peatlands are generally recognized as a substantial source of DOM to surface water (Mladenow et al., 2007; Clark et al., 2008; Thacker et al., 2008). Following the principle of "slow in and rapid out" (Körner, 2003), any potential restoration effects on the C cycles may only be observed following long-term studies (over several decades at least). Therefore, neither short-term nor medium-term data are able to show potential effects from changes to the biogeochemistry of peatland areas that have undergone long-term restoration.

Wallage et al. (2006) found that three years after fen blocking, the DOC concentrations were not only significantly lower than those of the adjacent drained fen, but also significantly lower than the DOC of an undrained fen. Worrall et al. (2007) found that the elevated concentrations of dissolved organic carbon (DOC) following peat drain-blocking only existed in the short-term (in the year after the blocking). Kalbitz et al. (2002) and Waddington et al. (2008) also found elevated DOC concentrations in peatlands that have been undergoing restoration for a few years. The long-term changes in DOC following successful peatland restoration, which includes the re-introduction of appropriate peatland vegetation and maintaining the water table close to the surface throughout the whole year, remain virtually unknown. In addition, the changes in dissolved organic matter (DOM) composition to peat restoration are poorly understood. Dissolved organic matter is a heterogeneous mixture of decomposition products reflecting its precursor material and environmental conditions (Kalbitz et al., 2000).

Ponnamperuma (1972) stated that under anoxic conditions fermentative metabolisms are dominant, promoting the production of DOC rather than the immediate production of $CO_2$. As a consequence, the enrichment of water-soluble intermediate metabolites can be assumed (Mulholland et al., 1990; Fiedler and Kalbitz, 2003; Sahrawat, 2004). Decomposition is generally prevented under anaerobic conditions (Moore and Dalva, 2001; Jungkunst et al., 2008), and metabolites such as acetate, formate, propionate, and lactate may accumulate. This might lead to higher DOC concentrations than those generated under aerobic conditions.

In degraded peatlands, greater peat decomposition resulted in low DOC concentrations in soil solution and groundwater (Kalbitz et al., 2002). In addition, the dissolved organic matter contained a larger portion of aromatic compounds than the DOM of more intact peatlands (Kalbitz et al., 2003). It is assumed that C mineralization is mainly fuelled by DOM, leaving behind the more refractory DOM components, i.e. aromatic and complex compounds (Kalbitz et al, 2003). The majority of these compounds are derived from lignin. Specific UV absorbance (e.g. 280 nm) and fluorescence spectroscopy can be used for the initial assessment of the contribution of aromatic and complex compounds to DOM (Kalbitz and Geyer, 2001; Kalbitz et al., 2003).

The present study focused on assessing the changes in the amount and composition of DOM to long-term peat restoration. A rewetted site and an adjacent drained site in the same peatland area were investigated. At the rewetted fen, the water table was re-established in 1984, i.e. 20 years before the present measurements were undertaken. We assumed the following:(1) the presence of higher DOC concentrations at the rewetted site was a result of anaerobic conditions; (2) a considerable depletion of aromatic and complex compounds at the rewetted site; and (3) a seasonality of DOC concentrations and DOM properties, i.e. higher DOC concentrations of DOC during summer than in winter as a result of higher microbial activity in the warmer months of the year. It was further hypothesized that the higher microbial activity during summer would result in an accumulation of DOM components that degrade only with difficulty, i.e. lignin-derived moieties with many aromatic and complex structures.

## 2. Materials and methods

### 2.1. Study sites

The study site 'Donauried' was previously presented in another study (Fiedler et al., 2008). The area is located at an altitude between 440 and 450 m a.s.l., with a mean annual temperature of 7.4 °C and a mean annual precipitation of 670 mm. The south western part of the Donauried (total area 47,150 ha) area comprises the largest coherent fen area (2987 ha) in southern Germany (LFU, 1999). Since the 19th century, the area has been intensively drained in order to be used for a broad range of purposes (as arable land, grassland, the excavation of peat and gravels, and as a drinking water reservoir). The historical peat layer (= 7 m) has gradually declined over the years. The average loss amounted to 7.2 mm $a^{-1}$ between 1951 and 1990 (Flinsbach et al., 1997), which is equivalent to 5.67 t C $ha^{-1}$ $a^{-1}$. The first nature conservation areas established for the protection of peat areas were created in 1966 and cover now 17% of the region's total fen area. The first attempts to regulate the water flow in drain ditches by weirs were made in 1972. Currently, an area of about 50 ha is being rewetted by way of leading the water flow into the drain ditches. In addition, water has been diverted from the nearby river since 1984 for rewetting purposes.

In the present study, a permanently drained site was compared with a site that was rewetted in 1984. Both sites were formerly used for peat extraction.

### 2.2. Measurements, sampling and analyses

For monitoring the ground water level (GWL) three PVC wells per site (1 m, diameter of 6 cm, Stockmann, Warendorf, Germany) were installed. The reduction–oxidation potential (Eh) was measured using platinum electrodes (5 replicates per depth) and an Ag/AgCl reference electrode (Fiedler et al., 2003). The soil temperatures were measured with thermocouples once per minute and automatically logged at hourly intervals (SITEC, Meeder, Germany). The hourly values were summarized as mean daily value.

In order to quantify the carbon content of DOM, i.e. DOC (dissolved organic carbon), freely drained pore water was collected using slit PVC pipes (length 10 cm, diameter 2.5 cm, 3 replicates per depth) coated with filter gauze (polypropylene, Eijkelkamp Agrisearch Equipment BV, Giesbeek, The Netherlands) and attached to a stainless-steel capillary (diameter 2 mm). The end of the capillary was closed using a three-way stop-cock (Fleischhacker GmbH & Co. KG, Schwerte, Germany). Pore waters were sampled using a syringe. Approximately 50 mL of water was sampled, transferred to a bottle and transported to the laboratory in a cool box, where the samples were filtered (0.45-µm, Macherey-Nagel GmbH & Co. KG, Düren, Germany). Prior to analysis, the samples were acidified (85% $H_3PO_4$). DOC was determined using a total C/N water analyser (DimaTOC 100, Dimatec Analysentechnik GmbH, Essen, Germany). All water probes were measured three times (error of measurement $\pm$ 1.7%).

The entire equipment was installed at depths of 5 (only Eh electrodes), 10, 20, 40 and 60 cm. GWL, Eh, temperature and DOC were monitored over one year (1st of April 2004 to 31th of March 2005).

The composition of DOM was analyzed in May, June, July, August and December 2004, and in January, February, and March 2005, representing a summer (soil temperature $>$10 °C) and a winter situation (soil temperature $<$5 °C) (Table 1). Specific UV absorbance values (280 nm, $SUVA_{280}$; UVIKON 930, BIO-TEK Instruments, Bad Friedrichshall, Germany) were corrected to 1 mg C $L^{-1}$. Additionally, synchronous fluorescence spectra (SFM 25, BIO-TEK Instruments, Bad Friedrichshall, Germany) were recorded and a humification index ($HIX_{syn}$) was calculated by dividing the intensity of the fluorescence bands or shoulders of a longer by a shorter wavelength (460 nm/ 345 nm; analytical error $<$ 2%). To prevent overestimation of these