Science of the Total Environment 586 (2017) 770–781

Contents lists available at ScienceDirect

Science of the Total Environment

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

Differences in DOM of rewetted and natural peatlands – Results from high-field FT-ICR-MS and bulk optical parameters

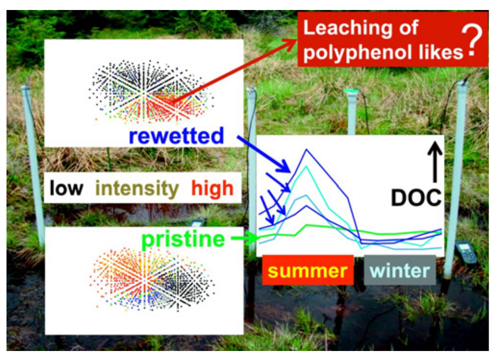
Peter Herzsprung [a,*], Katja Osterloh [c], Wolf von Tümpling [a], Mourad Harir [b], Norbert Hertkorn [b], Philippe Schmitt-Kopplin [b], Ralph Meissner [a,c], Sabine Bernsdorf [c], Kurt Friese [a]

[a] Helmholtz Centre for Environmental Research – UFZ, Brückstrasse 3a, 39114 Magdeburg, Germany
[b] Helmholtz Centre Munich, German Research Center for Environmental Health, Research Unit Analytical BioGeoChemistry (BGC), Ingolstädter Landstr. 1, 85764 Neuherberg, Germany
[c] Martin Luther University Halle-Wittenberg, Institute of Agricultural and Nutritional Sciences, Julius-Kühn Str. 23, 06112 Halle, Germany

HIGHLIGHTS

- Pristine peatland DOC and DOM quality was spatially and seasonally consistent.
- Rewetted peatland DOM showed spatial and seasonal inhomogeneity.
- FT-ICR-MS based inter sample rankings analysis identified differences in the chemical composition of DOM.
- DOC and HIX correlated with oxygen-rich and relatively unsaturated components.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 6 February 2017
Accepted 6 February 2017
Available online 16 February 2017

Editor: D. Barcelo

Keywords:
DOC
Fluorescence indices
Van Krevelen diagrams
Spatial resolution
Seasonality
Harz Mountains
Germany

ABSTRACT

Peatlands can be a potential source of dissolved organic matter (DOM) in fresh water catchment areas. The quantity and quality of DOM can differ between pristine, degraded and rewetted peatlands. Due to the large scale and continuing losses of peatlands, their conservation and restoration has been increasingly emphasized. Mostly rewetting measures are required to improve the hydrology of damaged peatlands, which is a precondition for the resettlement of peat-forming plant species. Thus, in term of DOM, there is a special need to understand how rewetting measures affect DOM characteristics and concentrations.

To estimate the potential leaching of humic substances from rewetted areas two natural sites were compared with four artificially rewetted sites in a peatland area of the Harz Mountains National Park, Germany. This was done with regards to DOM quality by combining the results from Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS, measured at one time in Spring) and excitation-emission-matrix fluorescence spectroscopy (EEMF, measured monthly for the period of one year).

The DOM quality was significantly less variable in the pristine peatland soil water compared to the rewetted peatland soil waters, from both a spatial and a seasonal perspective. The soil water from the rewetted peatland sites showed a higher degree of humification compared to pristine peatland. DOC concentration was mostly consistent in the pristine peatland over the year. The rewetted peatlands showed higher DOC levels in Summer months and lower DOC in Winter months compared to the pristine peatland.

It can be concluded that the rewetting of peatlands is coupled with high concentrations of DOC in soil water and its quality is highly aromatic (as reflected by the observed values from the humification index) during times with

* Corresponding author.
E-mail address: peter.herzsprung@ufz.de (P. Herzsprung).

http://dx.doi.org/10.1016/j.scitotenv.2017.02.054

elevated temperature. The results may have a significant input for dynamic catchment area studies with regards to rewetting peatland sites.

1. Introduction

Peatlands are key ecosystems in terms of carbon (C) storage. They represent the largest pool of terrestrial organic C (Gorham, 1991). While pristine peatlands predominantly act as sinks for atmospheric C over a longer period, degraded peatlands could become significant sources for organic soil C (Evans et al., 2016). This is caused by rapid peat decomposition processes due to oxygen-rich conditions at low water tables. Because natural peatlands offer several ecosystem services (e. g. nutrient retention, carbon sequestration, habitat for highly specialized species) the conservation, development and restoration of peatlands is necessary (Pfadenhauer and Grootjans, 1999). In this regard rewetting is a condition for the regeneration of degraded peatlands (Pfadenhauer and Grootjans, 1999; Meissner et al., 2008) as it helps to establish a water level regime appropriate for peat-forming key-species such as Sphagnum mosses and sedges (Tuittila et al., 2000; Rochefort et al., 2003).

Beside quantifying DOM quantities it is also important to characterize the composition of DOM. The latter determines how DOM reacts in the environment. DOM concentration and quality were followed in a peatland and forest headwater stream by Broder et al. (2016). They found seasonal differences in both DOM concentration and quality.

The effects of rewetting on dissolved organic matter (DOM) dynamics are not completely understood until now. Increasing (Zak and Gelbrecht, 2007; Strack et al., 2015) as well as decreasing (Frank et al., 2014; Höll et al., 2009; Wallage et al., 2006) dissolved organic carbon (DOC) concentrations and DOC loads were evidenced in connection with rewetting measures. Rewetting duration and its intensity influences vegetation composition and microbe composition as well as hydro-chemical conditions and processes due to the fact that hydrology (water table position and variation) influences oxygen availability and redox conditions. This may also have an important effect on DOC loads and dynamics (e.g. Frank et al., 2014) as well as hydrological and hydrochemical changes. Therefore particular attention should be paid to the variations of DOM in the soil waters of rewetted peatlands.

Most studies dealing with DOC dynamics in peatlands have shown seasonal variations in DOC concentrations (e. g. Schwalm and Zeitz, 2014, Osterloh et al., 2016). Seasonality in DOC concentration and additional DOM quality is often linked to biological and hydrological controls (Frank et al., 2014 e.g. temperature; D'Amore et al., 2010): variable plant productivity due to temperature-dependent growing periods (Strack et al., 2015; Freeman et al., 2004; Waddington et al., 2008), plant mixture (vascular plants versus mosses) (Strack et al., 2015), microbe activity (Höll et al., 2009), water table fluctuations (e.g. wet-dry-cycle) (Höll et al., 2009; Glatzel et al., 2006; Chow et al., 2006) and the variable contact time of water (precipitation, groundwater) with soil, and dilution strength as a function of precipitation rate and precipitation frequency (Fraser et al., 2001) as well as hydrological flow paths and flow conditions (Stutter et al., 2012).

DOC dynamics are potentially coupled to the leaching of humic substances in catchment areas. Such leaching can be a big issue in drinking water catchment areas for example. DOM does not pose a health risk itself but may become transformed into potentially harmful disinfection by-products (Reckhow et al., 1990; Beggs and Summers, 2011; Bull et al., 2011; Lavonen et al., 2013) when subjected to raw water processing, which often includes treatment with reactive species such as free chlorine or ozone. For these reasons, DOC-rich yellow-brown water incurs increased flocculation costs for to removing the precursors of unwanted organic byproducts (Lin et al., 2006). While raw water processing and the effects of DOM on catchment areas are not the issue this present study addresses, the question of potential leaching (from a qualitative point of view) of humic substances in rewetted peatland regions compared to pristine peatlands is of interest. One aspect of leaching may be the concentration and quality of DOM in soil waters.

FT-ICR-MS (Fourier transform ion cyclotron resonance mass spectrometry) was often applied for the characterization of DOM quality in soil waters. For example Roth et al. (2015) investigated DOM in soil waters from three different forest stands at three different seasons using FT-ICR-MS in order to study the control of DOM quality by pH. Ohno et al. (2014) investigated soil organic matter (SOM) and differentiated between deciduous and coniferous forest types with the analysis of water extractable organic matter via FT-ICR-MS in order to study the biodegradation of soil organic components. DOM quality was determined in fen and bog pore-waters in the Glacial Lake Agassiz Peatlands using FT-ICR-MS (D'Andrilli et al., 2010). Bogs and fens (in Stordalen Mire/Sweden) were also investigated by Hodgkins et al. (2014). They analysed DOM in soil pore-water using FT-ICR-MS to study the association of peat chemistry changes with greenhouse gas production (Hodgkins et al., 2014). Due to the relatively easy application compared to FT-ICR-MS, bulk optical parameters such as excitation-emission-matrix fluorescence (EEMF) were more commonly used for the characterization of soil water organic geochemistry. Inamdar et al. (2012) investigated soil water amongst other water bodies such as shallow groundwater, stream water, and hyporheic water in a forested mid-Atlantic watershed. They analysed fluorescent components using EEMF. Fellman et al. (2008) investigated fluorescence characteristics and the biodegradability of DOM in forest and wetland soil water. The dynamics of DOC were investigated on United Kingdom podzolic moorland by Stutter et al. (2012). They used specific UV absorption (SUVA) as a bulk optical parameter for the characterization of DOM quality in soil waters. In another study a farmed and a rewetted fen were compared with regard to DOC export (Schwalm and Zeitz, 2014). The authors did not sample soil water but water from ditches within the peatland area. Only a few studies have combined both analytical methods, e.g. the high resolution FT-ICR-MS and low resolution bulk optical parameters such as EEMF. Herzsprung et al. (2012) used Spearman's rank correlation to combine FT-ICR-MS elemental formula intensities with humic-like fluorescence intensities and found that oxygen-rich and relatively unsaturated components were highly fluorescent in the tributaries of a catchment area of a drinking water reservoir. Spearman's correlation was also used by Stubbins et al. (2014) to determine the elemental formula components associated with FDOM (fluorescent dissolved organic matter) in boreal rivers. The fluorescence index (FI) and humification index (HIX) were correlated to elemental formula intensities by Wagner et al. (2015) in tropical surface waters and by Lavonen et al. (2015) in Swedish water treatment plants.

While the analysis of DOM quality in soil waters was widely described as cited above using FT-ICR-MS or EEMF or in some cases a combination of both methods, a comparison of pristine peatlands with rewetted peatlands using seasonal DOC concentration and DOM quality measurements with both the above-mentioned analytical techniques combined has never been carried out before to the best of our knowledge. The renaturation or rather rewetting of formerly drained peatlands is a big issue, if the interests of nature protection and drinking water supply from reservoirs situated in affected catchment areas are considered. In our study we compared the DOC and DOM quality dynamics of soil waters from pristine and rewetted peatlands.

Here, we give a first insight in DOM quality differences in spatial and temporal dimensions in a nutrient-poor and acidic peatland named “Blumentopfmoor” in the Harz Mountains (central Germany). UV-spectra and EEMF spectra were determined once a month for one year (May 2013–April 2014) and were used to describe seasonal changes in DOM