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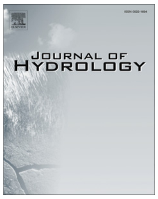

Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas

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SUMMARY

Accurate quantification of dissolved organic carbon (DOC) in surface and soil pore waters is crucial for understanding changes in water resources under the influence of climate and land use changes. Sampling and laboratory analysis of DOC content at a sufficient temporal frequency are especially difficult to achieve for natural DOC sources like the extensive boreal and arctic mire landscapes due to their remoteness. Therefore, the goals of this paper are (1) to investigate the performance of a portable, high-resolution ultraviolet–visible light spectroscopic method for determining the DOC content of surface and soil pore water samples from a boreal mire complex and (2) to compare the spectroscopic method with other DOC measurement techniques, e.g., the wet heated persulfate oxidation method and a laboratory, expulsion-based spectrophotometric method and (3) to assess different multivariate models that relate absorbance measurements with DOC contents. The study indicates that high-resolution spectroscopic measurements provide a simple, robust and non-destructive method for measuring DOC content. These measurements are of short duration (<1 min) and the sample analysis is portable, rendering this method particularly advantageous for in situ investigations at remote field locations. The study also demonstrates that if absorbances at specific wavelengths are used as proxies for DOC concentration, it is recommended to create site-specific calibration models that include more than one wavelength to achieve the optimal accuracy of the proxy-based DOC quantification.

1. Introduction

Recent efforts have been made to qualitatively and quantitatively characterize dissolved organic matter (DOM) in (near-) pristine and anthropogenically perturbed waterbodies (Ågren et al., 2008; Cory et al., 2011; Grayson and Holden, 2012; Freeman et al., 2001; Langergraber et al., 2004; Lauerwald et al., 2012; Ulanowski and Branfireun, 2013; Worrall et al., 2002, 2008). Several methods are available to determine the main component of DOM, i.e., the dissolved organic carbon (DOC) concentrations. Typically, the DOC content is determined by measuring the oxidation of organic matter to CO_2, which is generally accomplished using high-temperature combustion or persulfate oxidation (Aiken et al., 2002; Cory et al., 2011). Currently, special cuvette tests can be used to determine DOC content using the so-called expulsion method (e.g., LCK 385 and 386 test kits, Hach Lange GmbH, Germany; a detailed description of the expulsion method is presented in the method section). However, because these methods require bulky instruments, laboratory space and additional consumables, they cannot be directly used under field conditions. Such limitations make it particularly difficult to obtain frequent measurements in remote areas (e.g., Russian boreal mires), which often lack information concerning DOM changes in their surface and soil pore waters. Moreover, these methods only provide information about DOC concentrations; the characterization of DOM quality (e.g., molecular size), which is helpful to promote an improved understanding of DOM turnover processes and their environmental controls, cannot be accomplished without additional size fractionation (e.g., the use of tangential flow filtration, chromatographic analysis) (e.g., Guo and Santschi, 2007; Pereira et al., 2014; Pokrovsky et al., 2005, 2006, 2010; Shvartsev et al., 2012) or characterization with a light-based proxy (absorbance or fluorescent emission) (e.g., Ågren et al., 2008; Chen et al., 2003; Cory and McKnight, 2005; Thurman, 1985; Weishaar et al., 2003).

Because DOM has distinctive spectrophotometric properties and absorbs at a wide range of wavelengths in the UV and visible radiation spectra, a variety of spectroscopic techniques have been used to provide information about the bulk content and qualitative characterization of DOM (e.g., Baker and Spencer, 2004; Baker et al., 2008; Carter et al., 2012; Grayson and Holden, 2012; McKnight et al., 1997; Pastor et al., 2003; Tipping et al., 1988, 2009; Wallage and Holden, 2010; Weishaar et al., 2003; Worrall

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et al., 2002). However, the specific absorbance spectra of different DOM sources vary considerably. Thus, when using spectroscopic measurements as proxies for DOC concentrations, it is necessary to conduct a local calibration against one of the conventional DOC content determination methods (such as high-temperature combustion or persulfate oxidation). In the absence of site-specific calibration, the absorbance-based determination of DOC concentration can be inaccurate due to the varying absorbance strength of different types of DOM and the interference of other elements. For example, absorbance measurements can be influenced by dissolved nitrate and iron (Weishaar et al., 2003; Xiao et al., 2013). Advantageously, measurements made with spectrophotometers generally require a small sample size and are simple to perform. Due to recent technological developments, several advanced, "off-the-shelf" ultraviolet–visible light (UV–Vis) spectrometers are currently available to determine DOC levels under field conditions (e.g., ProPS-UV, Trios GmbH, Germany; CarboVis, WTW GmbH, Germany; and spectro::lyser, carbo::lyser and multi::lyser, s::can, Austria). The ability to operate an instrument in the field is particularly advantageous for environmental studies conducted in remote areas, which may lack laboratory space and equipment. Although these types of spectrometers are already widely used for effluent water-quality monitoring (e.g., Langergraber et al., 2004; Rieger et al., 2004), only a few studies within the geo-ecological sciences have used these probes (e.g., Waterloo et al., 2006; Koehler et al., 2009; Grayson and Holden, 2012; Jeong et al., 2012; Strohmeier et al., 2013).

Considering the importance of DOM in the carbon cycle, its influence on the cycling of other elements and its potential increase in concentrations under the influence of climate change and other anthropogenic factors, it is particularly important to obtain accurate and rapid estimates of DOC in remote areas. Hence, this study has the five following objectives:

1. To evaluate the performance of a portable UV–Vis spectrometer in measuring DOC concentration in surface and soil pore waters from a boreal mire complex under remote field conditions.
2. To compare the DOC content derived using high-resolution absorption spectrophotometry with the content derived from other available DOC measurement methods, such as the wet heated persulfate oxidation method and the expulsion method.
3. To assess the application of high-resolution absorbance measurements for determining DOC concentration using a set of different local calibration methods based on multiple stepwise regression (MSR), partial least-squares (PLS) regression, principal-component regression (PCR) and the two-component model of Carter et al. (2012).
4. To determine the wavelengths conferring an optimal explanatory power for different DOM size fractions that can be used as proxies to determine the DOC content.
5. To explore the specific spectrophotometric absorption properties of DOM in surface and soil pore waters in different land cover types within a boreal river valley mire complex that is typical for the extensive boreal lowland areas in Russia.

2. Materials and methods

2.1. Study site

The study was conducted on water samples collected from the Ust-Pojeg mire complex (61°56′N, 50°13′E, 119 m A.S.L.) in the Komi Republic (Fig. 1). This boreal river valley mire complex consisted of minerogenous (fen), ombrogenous (bog), and transitional forest-mire (marginal forest swamp) zones. The marginal forest swamp zone was located at the interface between the forest and mire zones and received water from both the mire and the forest mineral soils in addition to precipitation, the bog zone received water only from precipitation, and the fen zone was supplied by water from both precipitation and, marginally, from minerogenic throughflow. In the fen portion, excess water from snowmelt generates net outflow and high water tables, which is gradually reduced during the months April through July (Runkle et al., 2014). The vegetation cover varied among sites. The main species in the marginal forest swamp zone were *Picea obovata, Betula pendula, Alnus incana, Menyanthes trifoliata*, and *Sphagnum magellanicum*. The fen was predominantly vegetated with *Betula nana, Scheuchzeria palustris, Sphagnum spp.*, while the bog vegetation cover included mainly *Chamaedaphne calyculata, S. palustris, S. magellanicum* and *Sphagnum spp.* (Schneider et al., 2012).

The site's climate is boreal, humid and continental. The mean annual temperature was 1.1 °C for the period 1960–2011, and the mean annual precipitation at Syktyvkar for the period of 1973–1998 was 585 mm. The coldest month is January, and the warmest is July. The mean monthly air temperature is above 0 °C from April through October. Permanent snow cover begins at the end of October and continues until the beginning of April. Soils in all three investigated ecohydrological mire units were classified as Fibric Histosols according to the World Reference Base for Soil Resources (IUSS Working Group WRB., 2006; Langer, 2012). pH values varied among sites (outflow: 5.3; swamp-forest: 5.6; fen: 5.3; bog: 4.3). The details on hydrochemistry are presented in Table 1.

2.2. Sampling and filtration

Water samples were collected along a 1.2 km long transect in the south-western part of the Ust-Pojeg mire complex from bog, fen and marginal swamp areas and from the surface of the adjacent Pojeg River during several field campaigns from July 2010 to October 2011. The DOM fraction was separated using pre-combusted glass-fiber filters (0.7 μm GF/F, Whatman, UK) with a glass filtration set (Sartorius, Germany). Glass fiber filters were preferred for filtration because they are binder-free and do not add any contamination to the sample (Cory et al., 2011). To precondition the filtration system and avoid contamination from the filter prior to collecting samples, 30 ml of sample water was processed through the filter and then discarded. For further size fractionation, a tangential-flow filtration system was used to divide the overall bulk DOM fraction into two fractions: $\leqslant$1 kDa and $\leqslant$10 kDa, according to a protocol of Schwalger and Spitzy (2009). For tangential flow filtration, polyethersulfone cassette membranes (nominal molecular-size cut-offs of 1 kDa and 10 kDa, Omega, Centramate, PALL Corporation, USA) were used. The samples were then acidified with HCl to pH < 2 and stored at 4 °C until laboratory analysis. Samples with precipitated DOM particles were excluded from further analyses.

2.3. High-resolution spectroscopic measurements using a portable UV–Vis probe

A submersible, portable multi-parameter UV–Vis probe (spectro::lyser, s::can Messtechnik GmbH, Austria) was used for the high-resolution spectroscopic measurements. All of the controller's electronics, including the data logger, are placed in four tubular anodized aluminum housings. The length of the probe is approximately 0.6 m. The spectro::lyser measures absorbance across the UV–Vis range (200–750 nm, at 2.5 nm intervals) and saves these values in an internal datalogger. The measurement range of the probe depends on the optical path length, which can range from 2 to 100 mm. In this study, a probe with a path length of 5 mm was used, with the manufacturer's estimated DOC concentration measurement range of 0–84 mg L^{-1}. Duplicate DOC content