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Dissolved organic carbon and its potential predictors in eutrophic lakes

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ABSTRACT

Understanding of the true role of lakes in the global carbon cycle requires reliable estimates of dissolved organic carbon (DOC) and there is a strong need to develop remote sensing methods for mapping lake carbon content at larger regional and global scales. Part of DOC is optically inactive. Therefore, lake DOC content cannot be mapped directly. The objectives of the current study were to estimate the relationships of DOC and other water and environmental variables in order to find the best proxy for remote sensing mapping of lake DOC. The Boosted Regression Trees approach was used to clarify in which relative proportions different water and environmental variables determine DOC. In a studied large and shallow eutrophic lake the concentrations of DOC and coloured dissolved organic matter (CDOM) were rather high while the seasonal and interannual variability of DOC concentrations was small. The relationships between DOC and other water and environmental variables varied seasonally and interannually and it was challenging to find proxies for describing seasonal cycle of DOC. Chlorophyll *a* (Chl *a*), total suspended matter and Secchi depth were correlated with DOC and therefore are possible proxies for remote sensing of seasonal changes of DOC in ice free period, while for long term interannual changes transparency-related variables are relevant as DOC proxies. CDOM did not appear to be a good predictor of the seasonality of DOC concentration in Lake Võrtsjärv since the CDOM–DOC coupling varied seasonally. However, combining the data from Võrtsjärv with the published data from six other eutrophic lakes in the world showed that CDOM was the most powerful predictor of DOC and can be used in remote sensing of DOC concentrations in eutrophic lakes.

1. Introduction

Understanding of the true role of lakes in the global carbon cycle requires reliable estimates of dissolved organic carbon, DOC, as 90–95% of organic carbon in lakes is in the dissolved form (Wetzel, 2001). Monitoring of DOC in lakes is expensive and the extent of field sampling is limited, both spatially and temporally. Therefore, there is a strong need to develop remote sensing methods for mapping lake carbon content at larger regional and global scales (Kutser et al., 2015a).

Only the visible part of electromagnetic radiation can penetrate the water surface and give us information about water properties. Consequently, the parameter we want to measure from space or airborne sensors must affect the optical properties of water (e.g. reflectance), or correlate directly with water characteristics that affect the optical water properties (Kutser et al., 2015a). Coloured dissolved organic matter, CDOM, absorbs light and there is typically a strong correlation between DOC and CDOM in humic lakes where both parameters are fluctuating synchronously (Tranvik, 1990; Molot and Dillon, 1997; Kallio, 1999; Yacobi et al., 2003; Zhang et al., 2007; Erlandsson et al., 2012). Therefore, CDOM is often used as a proxy in mapping lake DOC content (Kutser et al., 2005; Del Castillo and Miller, 2008; Kutser et al., 2009). In non-humic lakes where DOC and CDOM do not vary synchronously the situation is much more complicated than in humic lakes. Molot and Dillon (1997) stated that if optical parameters are used as surrogates for all or some fraction of DOC, then the mathematical relationship between these parameters and the DOC fraction must be time invariant. There is a lack of data about the CDOM–DOC relationship in eutrophic lakes, where autochthonous DOC may form a considerable portion of the total DOC pool compared to

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allochthonous DOC (Toming et al., 2013). Autochthonous DOC is produced inside the lake by phytoplankton and other photosynthetic organisms. It does not absorb light and consists mainly of non-humic substances (Bertillson and Jones, 2003) that are labile and easily utilized or degraded by microorganisms (Thurman, 1985). Allochthonous DOC originates primarily from vascular plants and soil organic matter of the catchment area. It consists mainly of humic substances, is refractory to decomposition, absorbs light and is coloured brownish (Thurman, 1985). Thus, allochthonous DOC can be considered mainly as coloured (CDOM) and autochthonous mainly as non-coloured DOC due to their properties. Furthermore, the spatio-temporal dynamics of DOC and CDOM might differ largely due to their different sources, chemical composition, degradation processes (photochemical and microbial), discharge from rivers and other factors. Due to the high share of autochthonous DOC in eutrophic waters, CDOM might not be the best predictor for DOC.

Increases in DOC concentrations have often been detected in rivers and lakes (Evans et al., 2005; Clark et al., 2010; Filella and Rodríguez-Murillo, 2014) over the past decades. DOC plays a significant role in the carbon and energy cycle of lakes and as the main source of energy for microbial metabolism it can have a broad effect on food chains and on the proportions of auto- and heterotrophic processes (Tranvik, 1992). DOC also has an influence on nutrient retention and release and on the mobility of metals (De Haan, 1992). Moreover, the high concentration of organic acids in DOC gives a naturally low pH to the water of humic lakes (Kortelainen, 1999) and the photochemical degradation of DOC decreases oxygen concentration (Lindell and Rai, 1994). High levels of DOC must be removed from drinking water where it is to be disinfected using chlorination (Eikebrokk et al., 2004). Further, the coloured component of DOC – CDOM is one of the optically active substances in water competing with phytoplankton and other aquatic plants for the capture of available light energy. At the same time, CDOM protects aquatic organisms against harmful UV radiation (Kirk, 1980; Jones and Arvola, 1984; Davies-Colley and Vant, 1987; Arvola et al., 1999).

Thus, DOC is a very important parameter to monitor in water bodies and mapping both CDOM and DOC with remote sensing is an important task. On the other hand, the reasons described above indicate that other satellite products e.g. total suspended matter, turbidity, and transparency, could be used to predict lake carbon levels. Besides, CDOM may be one of the most difficult water quality variables to map with remote sensing (Brezonik et al., 2015). For providing efficient decision-making tools for lake managers and relevant input information for carbon cycle and climate models, it is important to understand all possible relationships of DOC with different water and environmental characteristics.

We have a unique 7-year database on DOC and other water and environmental variables in large, shallow and eutrophic Lake Võrtsjärv. This database makes it possible to explore the suitable predictors for DOC. Moreover, DOC, CDOM and Chl *a* data from Lake Võrtsjärv were analysed together with published data of the eutrophic lakes Balaton (Hungary), Taihu (China), Miastro (Belarus), Batorino (Belarus), Mendota (USA) and Kinneret (Israel) for large scale comparison.

Usually, regression models are used for quantifying the relationship between a dependent variable and the others on which it depends. In current study the traditional Pearson correlations, regression models and a novel predictive modelling technique called Boosted Regression Trees (BRT) were used in the analysis of the data. The BRT approach differs fundamentally from traditional regression methods that produce a single 'best' model, instead using the technique of boosting to combine large numbers of relatively simple tree models adaptively, to optimize predictive performance (e.g. Elith et al., 2006, 2008; Leathwick et al., 2006, 2008). The objectives of the current study are: (1) to estimate the correlative relationships of DOC and other water and environmental variables, and using BRT analyses (2) to clarify in which relative proportions different water and environmental variables determine DOC in Lake Võrtsjärv. Furthermore, DOC, CDOM and Chl *a* data from Lake Võrtsjärv were analysed together with published data of eutrophic lakes Balaton (Hungary), Taihu (China), Miastro (Belarus), Batorino (Belarus), Mendota (USA) and Kinneret (Israel) for large scale comparisons. We hypothesize that CDOM alone is not a good predictor for DOC in large, shallow and eutrophic lakes and that DOC correlations with other water parameters change in time and in the gradient of environment properties.

2. Material and methods

2.1. Study site

Data were analysed from a large, shallow, eutrophic Lake Võrtsjärv (57°50′–58°30′N and 25°35′–26°40′E), Estonia (Fig. 1). The lake area is 270 km^2, volume 0.75 km^3, mean depth 2.8 m, maximum depth 6 m, and catchment area is 3104 km^2. The water column is well mixed by surface waves and currents. The renewal of water takes 240–384 days and can differ markedly between dry and rainy years (Jaani, 1990). A specific feature of Võrtsjärv is the large natural climate-related variability of water level, which causes up to a 3-fold difference in its water volume (Nõges et al., 2010). The lake is covered by ice for an average 184 days. The ice-free period lasts from April to October and the ice period from November to March. The flow regimes of the inflowing rivers are natural, and discharges usually peak in April. The lake has 4 main inflows (the Rivers Väike Emajõgi, Õhne, Tarvastu, and Tänassilma) and one outflow (the River Emajõgi).

2.2. Data collection and analysis

We have a unique 7-year (from 2008 to 2014) database on DOC and other water and environmental variables in Lake Võrtsjärv: CDOM, chemical oxygen demand by permanganate (COD_{Mn}), water colour by Platinum-Cobalt scale ($colour_{Pt\text{-}Co}$), chlorophyll *a* (Chl *a*), total suspended matter (TSM), water temperature (WT), dissolved oxygen (O_2), water pH, Secchi depth (S), water level (WL), inflowing riverine discharges (I) and precipitation (PR). The data, aggregated with monthly time step were used in analysis. For those indices, which were measured daily (WL, cm; I, $m^3\ s^{-1}$; PR, mm) monthly averages were calculated prior to the analysis together with the indices which were measured once per month (DOC, mg C l^{-1}; CDOM, mg l^{-1}; COD_{Mn}, mg O l^{-1}; $colour_{Pt\text{-}Co}$, mg Pt l^{-1}; Chl *a*, mg l^{-1}; TSM, mg l^{-1}; WT, t°; O, mg l^{-1}; pH; S, m). WL, I, PR, COD_{Mn}, $colour_{Pt\text{-}Co}$, Chl *a*, TSM were measured as part of the state monitoring programme. These data were obtained from Estonian Environment Agency.

For determination of DOC concentrations, water was passed through pre combusted (3 h at 500 °C) Whatman GF/F glass microfiber filters and the carbon content of the filtrate was measured according to Toming et al. (2013).

The amount of CDOM was characterized by its concentration (mg l^{-1}) calculated from equation below (Eq. (1)) (Højerslev, 1980; Sipelgas et al., 2003):

$$C_{CDOM} = \frac{c^{*}{}_{f}(\lambda)}{\exp(-S(\lambda-\lambda_0))a^{*}{}_{CDOM}(\lambda_0)} \quad (1)$$

where $a^{*}{}_{CDOM}(\lambda_0)$ is the specific absorption coefficient of DOM,