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Patterns and predictability in the intra-annual organic carbon variability across the boreal and hemiboreal landscape

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HIGHLIGHTS

- We investigated the intra-annual variability in TOC concentration in 215 watercourses.
- Discharge and seasonality controlled most of the intra-annual variability.
- Catchment characteristics partly explained the controls.
- Climate change is likely to affect the intra-annual TOC variability.

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ABSTRACT

Factors affecting total organic carbon (TOC) concentrations in 215 watercourses across Sweden were investigated using parameter parsimonious regression approaches to explain spatial and temporal variabilities of the TOC water quality responses. We systematically quantified the effects of discharge, seasonality, and long-term trend as factors controlling intra-annual (among year) and inter-annual (within year) variabilities of TOC by evaluating the spatial variability in model coefficients and catchment characteristics (e.g. land cover, retention time, soil type). Catchment area (0.18–47,000 km^2) and land cover types (forests, agriculture and alpine terrain) are typical for the boreal and hemiboreal zones across Fennoscandia. Watercourses had at least 6 years of monthly water quality observations between 1990 and 2010. Statistically significant models ($p < 0.05$) describing variation of TOC in streamflow were identified in 209 of 215 watercourses with a mean Nash-Sutcliffe efficiency index of 0.44. Increasing long-term trends were observed in 149 (70%) of the watercourses, and intra-annual variation in TOC far exceeded inter-annual variation. The average influences of the discharge and seasonality terms on intra-annual variations in daily TOC concentration were 1.4 and 1.3 mg l^{-1} (13 and 12% of the mean annual TOC), respectively. The average increase in TOC was 0.17 mg l^{-1} $year^{-1}$ (1.6% $year^{-1}$).
Multivariate regression with over 90 different catchment characteristics explained 21% of the spatial variation in the linear trend coefficient, less than 20% of the variation in the discharge coefficient and 73% of the spatial variation in mean TOC. Specific discharge, water residence time, the variance of daily precipitation, and lake area, explained 45% of the spatial variation in the amplitude of the TOC seasonality.
Because the main drivers of temporal variability in TOC are seasonality and discharge, first-order estimates of the influences of climatic variability and change on TOC concentration should be predictable if the studied catchments continue to respond similarly.

1. Introduction

Factors controlling the total organic carbon (TOC) concentrations in watercourses are of great interest since TOC is a critical water quality characteristic that regulates primary production and living conditions for aquatic biota (Karlsson et al., 2009; Kullberg et al., 1993), and affects treatability of drinking water (Eikebrokk et al., 2004; Ledesma et al., 2012; Zeng and Arnold, 2013). Increasing long-term trends in annual mean TOC concentrations in watercourses across the northern hemisphere have received considerable attention (Monteith et al., 2007; Clark et al., 2010; Monteith et al., 2014). In addition to widespread

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changes in annual TOC concentration, there are also large intra-annual TOC variations (Winterdahl et al., 2014) that often exceed the year to year changes and yet have not been well studied. These rapid and large intra-annual (within year) changes are as important to aquatic life and drinking water treatability as long-term inter-annual (among years) changes. Questions remain about how patterns of intra-annual variation will respond to climate change.

Drivers of inter-annual trends in TOC include recovery from acidification due to decrease in anthropogenic sulfate (SO_4^{2-}) deposition (Monteith et al., 2007; de Wit et al., 2007), changes in temperature (Freeman et al., 2001; Sarkkola et al., 2009), changes in precipitation and discharge (Köhler et al., 2008; Ågren et al., 2008) as well as combinations of these (Futter et al., 2009; Erlandsson et al., 2008). Considering the factors influencing short-term variability on the intra-annual scale, discharge and temperature are often discussed (e.g. Dawson et al., 2008; Köhler et al., 2009). Sulfate concentration, which can be influenced by drought (Clark et al., 2006), seasonal climate anomalies (Lepistö et al., 2014) and the temperature of preceding seasons (Ågren et al., 2010), have also been identified as factors affecting TOC. Changes in short-term variation due to climate change may alter ecosystem functioning both through direct effect such as discharge and temperature, or changes in ecosystem response to climatic drivers.

That a limited number of hydro-climatic factors control a large amount of annual TOC variability provides a good basis for parameter parsimonious simulation of TOC at both intra-annual and inter-annual time scales. Different types of models have been used to estimate the TOC concentration in watercourses from parameter parsimonious models (e.g. Grieve, 1991; Boyer et al., 2000) to complex process-based models (Yurova et al., 2008; de Wit et al., 2007; Futter et al., 2007; Ledesma et al., 2012). The complex models aspire to capture the intricacies of how present and changing climate can influence catchment functioning. There is, however, a dearth of data against which to evaluate the hypothesized process interactions in such models and the associated parameters. Parameter parsimonious statistical models can be calibrated more systematically than more complex conceptual or process-based models, but they predict on the assumption that the ecosystem will behave in the future as it has in the past. Simpler approaches such as this can be useful for detecting if a system is changing over time (Gebrehiwot et al., 2013).

The aim of this study is to quantify the major influences on inter- and intra-annual TOC concentrations over decadal time scales across a large region using a standard load estimation modeling framework. This approach provides a unique opportunity to evaluate hypotheses about how catchment characteristics affect the intra-annual variability of TOC by using the spatial patterns in the model parameterizations.

To estimate TOC concentrations in watercourses over large spatial and long temporal time scales requires long-term monitoring data of TOC concentration and discharge measured in numerous watercourses throughout a region, as well as their catchment characteristics. TOC monitoring data from 215 watercourses was used to quantify intra-annual variability and trends in TOC. The watercourses are distributed across Sweden with catchments of different characteristics and sizes. The catchment data represent the primary land cover types found in the boreal and hemiboreal zone in all of Fennoscandia, including forested, agricultural, and alpine terrain. Parameter parsimonious regression models were applied to the TOC concentration data from all 215 watercourses, to evaluate how much of the intra- and inter-annual variations in TOC loadings (or export) could be explained by discharge, seasonality and long-term trend. The extent to which catchment characteristics can explain the spatial variation of the coefficients in the regression models was also quantified to gain understanding about what affects the TOC intra- and inter-annual variabilities. Whether the model residuals are stable over time was further evaluated to determine if catchment sensitivity to climate variables may be changing.

This work provides a systematic assessment of the influence of discharge, seasonality and long-term trend on intra- and inter-annual variations in TOC concentration of watercourses spanning a broad range of catchment size, land cover, latitude and climate. The application of a simple and consistent model specification to all watercourses is an important conceptual design element in this study and provides a uniform statistical approach for first quantifying intra- and inter-annual TOC variabilities and then assessing the major hydro-climatic and biophysical drivers of this variability across a diverse collection of catchments.

2. Materials and methods

2.1. Study area and model data sources

The TOC data and other water chemistry variables for watercourses throughout Sweden were obtained from the database of the Swedish national environmental monitoring program administered by the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences, SLU (Fölster et al., 2014). The sampling was conducted in accordance with international standard SS-EN ISO 5667–1:2007, edition 1. In large watercourses, every attempt was made to collect water from the middle of the stream by sampling from a bridge using a Ruttner water sampler. If this was not possible, samples were collected from the shore. In small watercourses, water was collected by a grab sample with the sampling bottle. All available sample data from watercourses having at least 6 years of monthly TOC data within the 21-year period from 1990 to 2010 were deemed sufficient for use in the study. TOC concentration and discharge data were available for the concentration estimation modeling from 215 watercourses across Sweden, including more than 42,500 water quality samples where TOC was observed. The study area covered most of the area of Sweden, spanning a latitudinal gradient from 55° to 68° N (Fig. 1a). The median length of time the data sets was 15 years, and 90% of the watercourses had 10 or more years of data. The watercourses had a range in mean TOC concentration from 1.4–25 mg l^{-1} (Fig. 1b). Catchments had a range in average air temperature from −2.0 to 8.8 °C (Fig. 1g); and a range in precipitation from 440 to 1270 mm per year (Fig. 1i). Temporal variation is reported as the coefficient of variance (CV, the standard deviation divided by the mean value) for TOC (Fig. 1c) and precipitation (Fig. 1j), and standard deviation (SD) is used for air temperature (Fig. 1h). The catchment areas range from 0.18 km^2 to over 47,000 km^2 (Fig. 1d). In order to keep observations independent, no nested subcatchments larger than a few percent of a downstream catchment area were included in the data set.

The TOC data were all analyzed at the national laboratory at the Department of Aquatic Sciences and Assessment using a Shimadzu TOC-VPCH analyzer. The dissolved organic carbon (DOC) concentration is not analyzed. In Swedish watercourses it has previously been shown that DOC and TOC generally differ by less than a few percent (Ivarsson and Jansson, 1994; Köhler, 1999; Laudon et al., 2011). Time series plots of the TOC data from all 215 watercourses were manually inspected and a total of 9 TOC concentration outliers were removed. These outliers were all isolated, exceptionally high values at least twice as high as any other value in the time series.

Daily discharge data (Fig. 1e and f) used in the TOC concentration-estimation models was computed by the Swedish Meteorological and Hydrological Institute (SMHI) using the Hydrological Predictions for the Environment (HYPE) model (Lindström et al., 2010; Strömqvist et al., 2012). When daily discharge modeled with HYPE was compared with daily observed values, the Nash-Sutcliffe efficiency (NSE, see Supplementary information S3) in the median watercourse was 0.68 and for long-term means the NSE was 0.997 for discharge and 0.92 for specific discharge with a median absolute error of 8% for both (Strömqvist et al., 2012). Time series of observed discharge between 1990 and 2010, gauged by SMHI was available at 59 of the 215 watercourses. These daily observed discharge data were used