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# Quantifying CDOM and DOC in major Arctic rivers during ice-free conditions using Landsat TM and ETM+ data

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## ABSTRACT

As high-latitudes warm, permafrost thaws, and the hydrological cycle accelerates, ground-based monitoring of riverine organic matter may be supplemented by satellite remote sensing during ice-free conditions. Recent programs, namely the Arctic Great Rivers Observatory, have established methodologically consistent sampling across the hydrograph, and shared the resulting data publicly. However, these efforts are limited by frequency, funding, and length of record. Satellite remote sensing can be used to estimate chromophoric dissolved organic matter (CDOM) as a riverine constituent that influences optical properties in surface waters. In this study, daily CDOM absorption was first estimated using discharge-constituent regression-based models for 2000–2013. We then regressed these discharge-based CDOM estimates against Landsat TM and ETM+ surface reflectance data from Google Earth Engine for the six largest rivers draining the pan-Arctic watershed (the Kolyma, Lena, Mackenzie, Ob', Yenisey, and Yukon rivers). These CDOM results were converted to dissolved organic carbon (DOC), using the strong relationship ($R^2 = 0.88$) between direct measurements of the two constituents. Using river-specific remote sensing models, $R^2$ could be as high as 0.84. Grouping all rivers into a single "universal" regression reduced $R^2$ and increased root mean square errors, such as in the Yenisey River where $R^2$ dropped by 0.63, and RMSE rose by 1.1 $m^{-1}$. Seasonally varying discharge drove much of the variation in satellite-derived CDOM and DOC, corroborating recent studies. Satellite imagery can increase the frequency of monitoring observations, particularly during summer and fall when riverine CDOM absorption may be most sensitive to thawing permafrost.

## 1. Introduction

Rivers transport over 3300 $km^3$ per year of water to the Arctic Ocean, representing ~10% of global riverine discharge annually into an ocean basin containing ~1% of global ocean volume (Aagard and Carmack, 1989; Menard and Smith, 1966). As such, terrestrial processes that impact the delivery of water and water-borne materials have the potential to strongly influence physical, chemical, and biological attributes of the Arctic Ocean. Riverine dissolved organic carbon (DOC) in particular is an important component of the Arctic carbon cycle, linking terrestrial and marine systems (Cooper et al., 2005; Holmes et al., 2012; Manizza et al., 2011). Dissolved organic matter (DOM) in major Arctic rivers is largely allochthonous, sourced from modern vegetation and a smaller fraction from ancient permafrost soils (Guo et al., 2012; Mann et al., 2012; Neff et al., 2006; Raymond et al., 2007). Impacts from rapid climate change, such as thawing permafrost (Frey and McClelland, 2009; Striegl et al., 2005), an accelerated hydrological cycle (White et al., 2007), and increased fire activity (Elmquist et al., 2008; Stubbins et al., 2015), influence the concentrations and composition of DOM in Arctic rivers. Recent studies have established that DOC from Arctic rivers can be highly labile (Frey et al., 2016; Gustafsson et al., 2011; Mann et al., 2015; Wickland et al., 2012), and losses of river-supplied DOC have been observed along Arctic shelves (Alling et al., 2010). These losses are likely driven by both biological utilization and photochemical interactions with chromophoric dissolved organic matter (CDOM) (Bélanger et al., 2006; Le Fouest et al., 2013; Stedmon et al., 2011), although the relative importance of these processes, and their interactions, remain to be determined. CDOM, the portion of the DOM pool that absorbs light at short wavelengths, is a useful proxy for DOC concentrations in many systems and is important for photochemical transformations (Hu et al., 2002; Spencer et al., 2012).

Although many questions remain about the fate of DOM in the

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coastal ocean, coordinated sampling efforts on the six largest Arctic rivers, initiated in 2003 (McClelland et al., 2008), have helped to better constrain estimates of fluvial export. Approximately 35 Tg of DOC is transported by Arctic rivers annually, of which ~15 Tg C are exported by the six largest Arctic rivers during the ice-free seasons (McGuire et al., 2010; Holmes et al., 2012). The Arctic Great Rivers Observatory (Arctic-GRO; 2009–present), originally established as the Pan Arctic River Transport of Nutrients, organic mattER, and suspended Sediments (PARTNERS; 2003–2007) project, samples the six largest Arctic rivers across the hydrograph. These rivers – the Kolyma, Lena, Mackenzie, Ob', Yenisey and Yukon – deliver over 50% of annual river discharge and DOC flux to the Arctic Ocean (Holmes et al., 2012). The multi-year datasets from PARTNERS/Arctic-GRO have been used to empirically model fluxes of dissolved and particulate constituents using the USGS Load Estimator (LOADEST) (Holmes et al., 2012; Mann et al., 2016; McClelland et al., 2016). The continued success of this approach, however, is contingent upon long-term funding of water discharge and biogeochemical measurements. LOADEST is a regression-based method that uses discharge-constituent relationships to model fluxes (Runkel et al., 2004), and these relationships can change over time. For example, Tank et al. (2016) defined separate DOC-discharge relationships for each decade to calculate fluxes in the Mackenzie River since the 1980s. Numerous studies in high-latitudes (Larouche et al., 2015) or large river systems (Mann et al., 2014) have tied DOC concentrations or CDOM absorption to important watershed processes (Worrall and Burt, 2010), even when discharge data is unavailable. Satellite remote sensing offers a method of monitoring Arctic rivers that, once established, is independent of discharge.

Satellite imagery has been used over the past decade to map CDOM remotely in a number of optically complex waters (Belanger et al., 2008; Brezonik et al., 2015; Fichot et al., 2013; Kutser, 2012; Menken et al., 2006). Although not originally designed for remote sensing of water quality, the Landsat Thematic Mapper and Landsat Enhanced Thematic Mapper Plus (Landsat TM and ETM+, respectively) have been used to estimate suspended sediment, chlorophyll, turbidity, and CDOM in lakes, rivers and the coastal ocean (Griffin et al., 2011; Joshi and Sa, 2015;Lymburner et al., 2016; Lobo et al., 2015; Olmanson et al., 2008). Landsat TM and ETM+ are limited by lower sensitivity and spectral resolution than ocean colour sensors or newer platforms such as Sentinel-2 or Landsat Operational Land Imager (OLI), making estimations of CDOM difficult in very dark waters with little water-leaving radiance (Kutser et al., 2005; Pahlevan and Schott, 2013; Palmer et al., 2015). Despite these limitations, the high spatial resolution and long-term dataset (1984–present) of Landsat TM and ETM+ make these sensors the best option for monitoring many inland waters (Kutser, 2012).

Here, we present an empirical approach relating CDOM in the six largest Arctic rivers to Landsat reflectance data. The regression-based models presented here represent the first pan-Arctic assessment of DOM in rivers from satellite remote sensing. Using Landsat imagery in conjunction with ground-based measurements of CDOM absorption and DOC concentrations, we estimated CDOM in the six largest Arctic rivers for 424 dates from May through October 2000–2013. We evaluate both "universal" and river-specific regressions, and compare our results to field-based measurements and regression-based discharge constituent models. As well, we examine whether relationships based on temporal variability can be spatially extrapolated.

## 2. Methods

### 2.1. Data collection and analysis

Field samples for model development were collected from the Kolyma, Lena, Mackenzie, Ob', Yenisey and Yukon rivers between 2003 and 2013 as part of the Arctic-GRO and PARTNERS projects (Fig. 1; www.arcticgreatrivers.org). Samples from 2014 to 2016 were used for independent validation of remote sensing models.

**Fig. 1.** Map of the Arctic Ocean drainage basin, with the watersheds of the six rivers included in this study. Red points are sampling locations on each river: Ob' at Salekhard, Yenisey at Dudinka, Lena at Zhigansk, Kolyma at Cherskiy, Yukon at Pilot Station, and Mackenzie at Tsiigehtchic. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Depth-integrated cross-sectional sampling was conducted at downstream locations on each river, capturing 96% of drainage from their combined watersheds, a total of 10.9 million km$^2$ (Holmes et al., 2012). Comparisons of surface samples and depth-integrated samples from the Arctic-GRO/PARTNERS sites have demonstrated that DOC and other dissolved constituents are evenly distributed throughout the water column at these sites (Holmes et al., 2012; Raymond et al., 2007). For more details on sample collection, see previous publications from Arctic-GRO/PARTNERS (Holmes et al., 2012; Raymond et al., 2007; Walker et al., 2013). Sampling campaigns from 2004 to 2011 explicitly addressed the highly seasonal nature of Arctic rivers, with targeted sampling during spring freshet, throughout the ice-free period, and during winter under the ice (McClelland et al., 2008). From 2012 – present, sampling occurred on each river every other month. Additional samples, used in this study for further model evaluation, were collected during field campaigns to the Mackenzie (2011) and Kolyma (2013) rivers, in the spring shortly after ice break-up on each river. These surface samples, from approximately 0.5 m depth, were collected and stored in polycarbonate or HDPE bottles, 1–2 L volume, and processed within hours of collection.

Arctic-GRO and PARTNERS DOC and CDOM samples were filtered within 2–4 h of sample collection through 0.45 μm Geotech medium or high capacity capsule filters into pre-cleaned, pre-rinsed HDPE bottles and shipped frozen to the Woods Hole Research Center (WHRC). DOC samples from PARTNERS (2003–2006) were measured for concentration at the National Ocean Sciences Atomic Mass Spectrometry (AMS) facility at Woods Hole Oceanographic Institute or the AMS facility at University of Arizona (Holmes et al., 2012; Raymond et al., 2007). All Arctic-GRO DOC samples were measured at the WHRC using a Shimadzu (TOC-V) organic carbon analyzer. Absorbance was measured at WHRC using a dual-beam Shimadzu UV-1800 with a 1 cm quartz cuvette, from wavelengths 200–800 nm at 1 nm intervals against nanopure water with ± 0.4%. Owing to logistical constraints, these measurements were made using frozen water samples which can lead to changes