Utilizing Colored Dissolved Organic Matter to Derive Dissolved Black Carbon Export by Arctic Rivers

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The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest

Author contribution statement

All authors contributed to the design of the study. JN analyzed samples for dissolved black carbon. AS, RGMS, and PJM conducted modeling studies. All authors contributed to the writing of the manuscript.

Keywords

Carbon Cycle, Arctic, black carbon, Colored dissolved organic matter (CDOM), Climate Change, Rivers, hydrology

Abstract

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Wildfires have produced black carbon (BC) since land plants emerged. Condensed aromatic compounds, a form of BC, have accumulated to become a major component of the soil carbon pool. Condensed aromatics leach from soils into rivers, where they are termed dissolved black carbon (DBC). The transport of DBC by rivers to the sea is a major term in the global carbon and BC cycles. To estimate Arctic river DBC export, 25 samples collected from the six largest Arctic rivers (Kolyma, Lena, Mackenzie, Ob', Yenisey and Yukon) were analyzed for dissolved organic carbon (DOC), colored dissolved organic matter (CDOM), and DBC. A simple, linear regression between DOC and DBC indicated that DBC accounted for 8.9 ± 0.3% DOC exported by Arctic rivers. To improve upon this estimate, an optical proxy for DBC was developed based upon the linear correlation between DBC concentrations and CDOM light absorption coefficients at 254 nm (a254). Relatively easy to measure a254 values were determined for 410 Arctic river samples between 2004 and 2010. Each of these a254 values was converted to a DBC concentration based upon the linear correlation, providing an extended record of DBC concentration. The extended DBC record was coupled with daily discharge data from the six rivers to estimate riverine DBC loads using the LOADEST modeling program. The six rivers studied cover 53% of the pan-Arctic watershed and exported 1.5 ± 0.1 million tons of DBC per year. Scaling up to the full area of the pan-Arctic watershed, we estimate that Arctic rivers carry 2.8 ± 0.3 million tons of DBC from land to the Arctic Ocean each year. This equates to ~8% of Arctic river DOC export, slightly less than indicated by the simpler DBC vs DOC correlation-based estimate. Riverine discharge is predicted to increase in a warmer Arctic. DBC export was positively correlated with river runoff, suggesting that the export of soil BC to the Arctic Ocean is likely to increase as the Arctic warms.

Ethics statement

(Authors are required to state the ethical considerations of their study in the manuscript including for cases where the study was exempt from ethical approval procedures.)

Did the study presented in the manuscript involve human or animal subjects: No

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Keywords: Carbon Cycle, Arctic, Black Carbon, Colored Dissolved Organic Matter (CDOM), Climate Change, Rivers, Hydrology.

Abstract

Wildfires have produced black carbon (BC) since land plants emerged. Condensed aromatic compounds, a form of BC, have accumulated to become a major component of the soil carbon pool. Condensed aromatics leach from soils into rivers, where they are termed dissolved black carbon (DBC). The transport of DBC by rivers to the sea is a major term in the global carbon and BC cycles. To estimate Arctic river DBC export, 25 samples collected from the six largest Arctic rivers (Kolyma, Lena, Mackenzie, Ob', Yenisey and Yukon) were analyzed for dissolved organic carbon (DOC), colored dissolved organic matter (CDOM), and DBC. A simple, linear regression between DOC and DBC indicated that DBC accounted for 8.9 ± 0.3% DOC exported by Arctic rivers. To improve upon this estimate, an optical proxy for DBC was developed based upon the linear correlation between DBC concentrations and CDOM light absorption coefficients at 254 nm (a_{254}). Relatively easy to measure a_{254} values were determined for 410 Arctic river samples between 2004 and 2010. Each of these a_{254} values was converted to a DBC concentration based upon the linear correlation, providing an extended record of DBC concentration. The extended DBC record was coupled with daily discharge data from the six rivers to estimate riverine DBC loads using the LOADEST modeling program. The six rivers studied cover 53% of the pan-Arctic watershed and exported 1.5 ± 0.1 million tons of DBC per year. Scaling up to the full area of the pan-Arctic watershed, we estimate that Arctic rivers carry 2.8 ± 0.3 million tons of DBC from land to the Arctic Ocean each year. This equates to ~8% of Arctic river DOC export, slightly less than indicated by the simpler DBC vs DOC correlation-based estimate. Riverine discharge is predicted to increase in a warmer Arctic. DBC export was positively correlated with

river runoff, suggesting that the export of soil BC to the Arctic Ocean is likely to increase as the Arctic warms.

1.Introduction

Fire occurs in nearly all terrestrial ecosystems (Bowman et al., 2009) and is on the increase in the Arctic (Higuera et al., 2008;Hu et al., 2010). Black carbon (BC) refers to thermally altered organic material and it comes in many forms (Forbes et al., 2006), ranging in chemistry from minimally charred biomolecules (Myers‐Pigg et al., 2015) to condensed aromatics formed at high temperatures (Dittmar, 2008). Once formed, condensed aromatics are ultra-refractory within soils, being preferentially preserved for hundreds to thousands of years (Schmidt et al., 2011). This stability, together with the ubiquity of fire, has resulted in condensed aromatics being distributed throughout the world's soils (Forbes et al., 2006;Guggenberger et al., 2008), where they have accumulated to represent approximately 10% of the global soil carbon store (Mitra et al., 2013). Wildfires have burned since the emergence of land plants 420 million years ago (Bowman et al., 2009). Without a significant loss term, condensed aromatics should have accumulated to represent an even greater pool of soil carbon than currently observed. The mobilization of soil condensed aromatics into solution and subsequent export by rivers to the oceans is the main loss term identified to date (Guggenberger et al., 2008;Dittmar et al., 2012a;Jaffé et al., 2013).

Once in solution, condensed aromatics are termed dissolved black carbon (DBC) (Dittmar, 2008) and their export through rivers links the soil BC store to another major global carbon store, that of dissolved organic carbon (DOC) in the oceans (Hansell, 2013). As in soils, DBC in the oceans appears to be highly bio-refractory, based upon its ancient apparent radiocarbon age (Ziolkowski and Druffel, 2010), and has accumulated to be major pool of global carbon (>12,000 Tg-C; Tg-C = 10^{12} grams of carbon) (Dittmar and Paeng, 2009). Deep sea hydrothermal systems (Dittmar and Paeng, 2009) and atmospheric deposition (Jurado et al., 2008) have been proposed as sources of oceanic DBC. However, rivers are currently the major identified source of DBC to the ocean, delivering an estimated 26.5 Tg of DBC per year (Jaffé et al., 2013). Photo-degradation by sunlight is the major identified sink for DBC (Stubbins et al., 2010;Stubbins et al., 2012). However, at depth in the ocean, DBC behaves almost conservatively, suggesting minimal loss when light is not present (Dittmar and Paeng, 2009). Therefore, if DBC can reach areas of deep water formation before being photo-degraded, it may be in essence reburied in the deep ocean.

In this manuscript we present data for DBC concentrations in major Arctic rivers and estimate annual export of DBC from Arctic soils to the Arctic Ocean. While riverine inputs of DOC to the Arctic Ocean are well constrained (Raymond et al., 2007;Spencer et al., 2009;Holmes et al., 2012), this is the first estimate of DBC export to the Arctic Ocean. To make this estimate, we quantified DBC in depth and flow integrated samples collected near the mouths of the six largest Arctic rivers under variable hydrological conditions (Figure 1; Kolyma, Lena, Mackenzie, Ob', Yenisey and Yukon). Together, these six river watersheds cover 53% of the pan-Arctic watershed (Holmes et al., 2012). Discharge varies markedly with season in Arctic rivers. In winter, November to April, the watersheds and river surfaces are frozen such that groundwater derived discharge dominates, and only 10 to 15% of the annual Arctic river DOC load is exported during this six month period (Holmes et al., 2012). With the warmth of spring, thawing winter snow and ice drive a massive discharge peak that is accompanied by highest annual DOC concentrations. As a consequence, typically 45 to 65% of the annual Arctic DOC

load is exported during May and June, the two months of the spring freshet (Raymond et al., 2007;Spencer et al., 2009;Holmes et al., 2012). After the intense spring freshet, the months from July through October account for the remainder of the annual DOC export.

In the current study, DBC was quantified in 25 samples, collected over a broad range of runoff values in 2009. We also determined the Naperian light absorption coefficient of colored DOM (*a*CDOM; m^{-1}), an optical property of DOM that is a good proxy for the aromatic components of the DOM pool (Weishaar et al., 2003;Stubbins et al., 2008;Spencer et al., 2009), including DBC (Stubbins et al., 2012). *a*CDOM was determined for 410 samples spanning the seasonal hydrographs of each river and seven years (2004 to 2010). The utility of *a*CDOM as a proxy for DBC within Arctic rivers was confirmed and used within a LOADEST modelling exercise to develop a robust estimate for DBC export to the Arctic Ocean.

2.Methods

2.1 Sample collection and processing

Sample sites for each river were as follows, Salekhard (Ob'), Dudinka (Yenisey), Zhigansk (Lena), Cherskiy (Kolyma), Pilot Station (Yukon) and Tsiigehtchic (Mackenzie). Discharge data (m^3 sec^{-1}) was taken from the ArcticRIMS website (http://rims.unh.edu/data.shtml) for nearby gauging stations and converted to surface area normalized runoff (m^3 km^{-2} sec^{-1}; Table S1). The gauging stations and sampling locations are near the mouths of the rivers, capturing 96% of the six rivers combined watershed area (Figure 1; Table 1). Depth integrated, flow weighted samples were collected following US Geological Survey protocols, filtered through pre-cleaned capsules (0.45 μm; Geotech), placed in acid-soaked Nalgene polycarbonate bottles and frozen until further processing (Holmes et al., 2012).

2.2 Dissolved organic carbon concentrations

Aliquots of sample were transferred to pre-combusted 40 mL glass vials, acidified to pH 2 (hydrochloric acid), and analyzed for non-purgable organic carbon using a Shimadzu TOC-VCPH analyzer fitted with a Shimadzu ASI-V autosampler. In addition to potassium hydrogen phthalate standards, aliquots of deep seawater reference material, Batch 10, Lot# 05-10, from the Consensus Reference Material Project (CRM) were analyzed to check the precision and accuracy of the DOC analyses. Analyses of the CRM deviated by <5% from the reported value for these standards (41 to 44 μM-DOC; http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.htm). Routine minimum detection limits in the investigator's laboratory using the above configuration are 2.8±0.3 μM-C and standard errors are typically 1.7±0.5% of the DOC concentration (Stubbins and Dittmar, 2012).

2.3 Colored dissolved organic matter Naperian light absorption

Sample was placed in a 1 cm quartz absorbance cell situated in the light path of an Agilent 8453 ultraviolet-visible spectrophotometer and sample CDOM absorbance spectra were recorded from 190 to 800 nm. Ultrapure water (Milli-Q) provided a blank. Blank corrected absorbance spectra were corrected for offsets due to scattering and instrument drift by subtraction of the average absorbance between 700 and 800 nm (Stubbins et al., 2011). Data output from the spectrophotometer were in the form of dimensionless absorbance (i.e. optical density, OD) and were subsequently converted to the Napierian absorption coefficient, a (m^{-1}) (Hu et al., 2002).

2.4 Dissolved black carbon concentration and quality

Freeze dried river water samples were analyzed for DBC. DBC was determined at the molecular level via the benzenepolycarboxylic acid (BPCA) method as described in (Dittmar, 2008) and with modifications following (Stubbins et al., 2012). In brief, ~2 μmol of freeze dried DOC was transferred into pre-combusted (400°C, 4 hours) 1 mL glass ampoules, and then redissolved in 500 μL of nitric acid (65%). The ampoules were sealed and heated to 170°C in a stainless steel pressure bomb inside a furnace for 9 hours. After the ampoules cooled, 450 μL was transferred into 1 mL maximum recovery vials (Waters). The nitric acid was evaporated in a centrifugal evaporator (RVC 2-18, Christ, Germany) and the samples were redissolved in 100 μL of phosphate buffer solution (Na_2HPO_4 and NaH_2PO_4 each 5 mM in ultrapure water, buffered pH 7.2). BPCAs were determined on a Waters ACQUITY UPLC (Ultra Performance Liquid Chromatography) system composed of a binary solvent manager, a sample manager, a column manager and a photodiode array light absorbance detector (PDA eλ). BPCAs were separated on a Waters ACQUITY UPLC BEH C18 Column (2.1 x 150 mm, 1.7 μm) with an aqueous phase / methanol gradient. The aqueous phase consisted of a tetrabutylammonium bromide solution (4 mM, ACS quality) in phosphate buffer (Na_2HPO_4 and NaH_2PO_4 each 5 mM in ultrapure water, pH 7.2). The injection volume was 10 μL. BPCAs were identified according to retention time and absorbance spectra (220 to 380 nm). Quantification was performed using the absorption signal at 240 nm and external calibration.

DBC concentrations were calculated from the detected BPCA concentrations. The original equation to estimate DBC in nM of carbon (nM-C), from the molar BPCA concentrations of each BPCA (nM) (Dittmar, 2008) was:

$$[DBC] = 33.4([B6CA]+[B5CA]+0.5[B4CA]+0.5[B3CA]) \quad (1)$$

The factor of 33.4 is based upon a conservative estimate of the average number of C atoms within DBC molecules identified by FT-ICR MS in a variety of natural waters (Dittmar, 2008). Note that the [DBC] is in nM-C and the BPCA concentrations are reported in nM of each molecule. Each BPCA is constituted of several C atoms. For instance, B6CA includes the 6 Cs in the aromatic ring, plus 6 carboxyl group (COOH) Cs. Therefore, the conversion factor of 33.4 represents a factor of approximately 3 on a carbon basis. This compares with factors of 2.27 in an early study that assessed the yield of BPCAs from solid charcoals (Glaser et al., 1998) and a factor of 4 suggested for aquatic samples (Ziolkowski and Druffel, 2010;Ziolkowski et al., 2011). Under certain oxidation conditions the nitric acid oxidation of BC to BPCAs can yield nitrated analogs of the BPCAs that are not quantified here, but do constitute part of the DBC pool (Ziolkowski et al., 2011). Thus, the total DBC concentrations reported here represent a conservative estimate of total DBC in aquatic systems given that the conversion factor was lower than used elsewhere and nitrated-BPCAs were not included in the analysis.

The method used here as originally presented utilized each of the BPCAs to calculate [DBC] via equation 1 (Dittmar, 2008). Although B3CAs were reported to be stable at 170°C (Dittmar, 2008), subsequent experience suggests that recoveries of B3CAs are not always 100% (Stubbins et al., 2012). Furthermore, 1,2,4,5-B4CA is the only B4CA that is commercially available as a standard, prohibiting the confident conversion of the absorption signal at 240 nm for the other B4CAs to quantities. Therefore, as in a previous study (Stubbins et al., 2012), total DBC concentrations here were calculated directly from the robustly quantified B5CA and B6CA concentrations. An extensive BPCA data set collected for the Southern Ocean (Dittmar and Paeng, 2009), the Gulf of Mexico (Dittmar et al., 2012b) and other regions (unpublished) was used to develop a power-function relationship ($R = 0.998$, $n = 351$, $p < 0.0001$; Figure on Data

Sheet S1) to predict the concentration of DBC from the sum of the quantitatively dominant and robustly quantified B5CA and B6CA. This extrapolation reduced the analytical error range of replicate analysis for the calculation of total DBC within the model dataset to below 2% and provided a method to compare the data reported here with the total DBC concentrations reported elsewhere (Dittmar, 2008;Dittmar and Paeng, 2009;Dittmar et al., 2012a;Jaffé et al., 2013).

Given the differences in oxidation conditions and conversion factors applied in the literature, we also report the concentrations of the individual BPCAs to enable comparison with other datasets (Table S1).

3. Results

The six rivers were sampled at variable discharge (Table S1). Concentrations of DOC ranged from 2.6 to 17.5 mg-C L^{-1}, and a_{254} from 12 to 148 m^{-1}. Concentrations of each BPCA quantified are listed in Table S1. B5CA was the most abundant BPCA and total DBC concentrations ranged from 0.14 to 1.51 mg-C L^{-1}. Changes in the quality of DBC being exported were also evident, with the B6CA:B5CA ratio ranging from 0.16 to 0.43 (Table S1). DBC loads on days when DBC concentrations were measured (i.e. DBC concentration × daily discharge) varied from 0.26 to 194.5 kg sec^{-1} (Table S1). Within each river, the concentrations and loads of DBC were highest during peak discharge.

4.Discussion

4.1 Dissolved black carbon concentrations

DBC concentrations varied by over an order of magnitude, from 0.14 to 1.51 mg-C L^{-1} (Table S1). For comparison, reported DBC concentrations ranged from 0.002 to 2.77 mg-C L^{-1} in global rivers (Jaffé et al., 2013) and from 0.02 to 0.88 mg-C L^{-1} in a small Arctic stream (Guggenberger et al., 2008). Upper limits to the concentrations of highly bio-labile forms of thermogenic DOC have been estimated in the Siberian rivers studied here based upon concentrations of levoglucosan (Myers-Pigg et al., 2015). These highly bio-labile forms of thermogenic contribute up to 0.1 to 0.3 mg-C L^{-1} to the DOC pool at the sites studied here (data from 2004-2006) (Myers-Pigg et al., 2015).

Previous work in the Arctic has demonstrated a strong link between DOC concentration and river hydrology. Early in the year, under ice flow cannot access the organic-rich seasonally thawed soil layer. Consequently, DOC concentrations in the river are low and sourced from groundwater (Table S1) (Holmes et al., 2012). In the spring, soils and waterways thaw, and the spring freshet inundates the watershed. DOC concentrations reach maxima during this flushing event and subsequently decline as water levels fall (Holmes et al., 2012). For DBC, the same trend of high concentration at high flow, is apparent in the regression of DBC concentrations versus runoff (watershed area normalized discharge; $m^3\,km^{-2}\,sec^{-1}$; Table S1), which reveals a significant linear correlation across the 6 rivers studied (Figure 2A; $R^2 = 0.63$; $n = 25$; $p < 0.0001$).

Plots of solute concentration versus runoff are used in hydrological studies to learn more about potential solute sources and the mechanisms controlling their export (Evans and Davies, 1998). The simplest interpretation of the linear correlation between DBC and runoff requires the conservative mixing of only two sources. In the Paraíba do Sul River, Brazil, variations in DBC concentrations with hydrology were explained by a simple two endmember model, with low DBC concentrations in groundwater under base flow conditions mixing with inputs of higher, but

constant DBC concentration waters from active soil layers as discharge increased (Dittmar et al., 2012a). In Arctic rivers, the relationship between hydrology and DBC concentration also indicates that in the winter, when the watersheds are frozen and discharge at a minimum, rivers are dominated by inputs from groundwater with low DBC. As runoff increases in the spring, the hydrological pathway incorporates soil active layers, which are rich in organics, including soluble BC (Guggenberger et al., 2008).

The lack of a plateau at high runoff in the current dataset (Figure 2A) suggests that if runoff were to increase, then DBC concentrations would also continue to increase, leading to greater DBC export. Eurasian Arctic river discharge has increased (Peterson et al., 2002). Modelling studies predict that runoff will increase further as the Arctic warms in the future, with the greatest increases occurring as an amplification of the spring freshet (Van Vliet et al., 2013). If these models are correct, Figure 2A suggests DBC exports will also increase, with the spring freshet contributing ever more to annual DBC loads. Thus, both the magnitude and the timing of DBC delivery to the Arctic Ocean are liable to change in the future.

4.2 Dissolved black carbon quality

The molecular BPCA method as applied here quantifies broad classes of DBC oxidation products, each with a different number of carboxylic groups (Dittmar, 2008). These are the: benzeneTRIcarboxylic acids (B3); benzeneTETRAcarboxylic acids (B4); benzenePENTAcarboxylic acid (B5); and, benzeneHEXAcarboxylic acid (B6). Each of these BPCAs provides structural information about DBC. B6 is indicative of highly condensed aromatics, whereas the benzene products with lower numbers of carboxylic substitutes are indicative of molecules with smaller numbers of condensed rings at their core (Schneider et al., 2010). As B6 and B5 were the most robustly quantified BPCAs, only the ratios of these two BPCAs are reported. The B6:B5 ratio provides an index, where higher values indicate greater levels of the most condensed forms of DBC (Stubbins et al., 2012). B6:B5 ratios have been reported for Little Grawijka Creek, a small Arctic stream (watershed area 0.44 km^2) (Guggenberger et al., 2008) within the watershed of the Yenisei River (watershed area 2.54×10^6 km^2; Table 1). Comparison of B6:B5 values for the 6 large Arctic rivers (0.16 to 0.43; Table S1) to values in the Little Grawijka Creek (0.30 to 0.65) (Guggenberger et al., 2008) suggests the DBC within the mainstems of the large Arctic rivers may be less condensed than DBC in Little Grawijka Creek, and possibly other Arctic headwaters.

In the Siberian rivers (Kolyma, Lena, Ob' and Yenisey), there was a significant correlation between B6:B5 and runoff (Figure 2B). The logarithmic fit indicates that at low flow, these Siberian rivers are dominated by water from a source with low concentrations of DBC (Figure 2A) and that the DBC in this water is less condensed than the DBC exported at high runoff (Figure 2B). The B6:B5 ratio then approaches a plateau at high runoff, where the value reached at the plateau can be considered the B6:B5 ratio of a putative high runoff, high DBC concentration endmember derived from the soil active layer. The logarithmic fit to the data (Figure 2B caption) suggests this endmember would have a B6:B5 ratio of 0.63, a value similar to the highest B6:B5 ratio observed at peak discharge during the spring freshet within Little Grawijka Creek (0.65) (Guggenberger et al., 2008).

Although future work is required to determine the source of DBC to Arctic rivers, in the current study, both the concentrations (Figure 2A) and the degree of DBC condensation (Figure 2B) were elevated in the Siberian rivers during high flow, suggesting a soil source. It is unclear why this trend in B6:B5 was not apparent in the Yukon and Mackenzie Rivers of Northern America. The significantly higher sediment loads and associated sorption reactions in the North

American rivers (Holmes et al., 2012) may differentiate their B6:B5 ratios from those observed in the sediment-poor Siberian rivers. Within the Mackenzie, B6:B5 ratios may also be influenced by inputs from petrogenic sources (Yunker et al., 2002). More data is required to verify these trends and, once verified, to seek mechanistic explanations.

4.3 Estimating dissolved black carbon export from dissolved organic carbon

DBC and DOC concentrations were correlated ($R^2 = 0.96$; Figure 3A). Previous work has reported similar correlations between total DOC and DBC concentrations within rivers. For instance, Jaffe *et al.* (2013) conducted an assessment including 109 DBC concentrations for rivers diverse in stream order and latitude, including seasonally averaged values for the DBC values of the 6 Arctic rivers studied here (i.e. data for each of the 25 samples analyzed here were not presented in Jaffe et al. (2013), only their averages on a river-by-river basis). As in the current study, the intercept of the slope between DBC and DOC was statistically indistinguishable from zero (current study intercept = -0.019 ± 0.035 mg-C L^{-1}). Therefore, Jaffe *et al.* (2013) interpreted the slope of the linear regression to approximate the globally averaged contribution of DBC to riverine DOC concentrations. For their dataset, DBC was estimated to account for 10.5±0.7% of global DOC exports. Following the same approach, reference to the slope in Figure 3A indicates that DBC constitutes 8.9±0.3% of Arctic river DOC. This suggests Arctic river DOC is slightly depleted in DBC relative to rivers globally, though larger datasets for both global and Arctic rivers are required to strengthen this conclusion. Jaffe *et al.* (2012) used the percentage contribution of DBC to riverine DOC concentrations and a global DOC load of 250 Tg-C yr^{-1} (Hedges et al., 1997) to estimate that 26.5 ± 0.8 Tg-C yr^{-1} of DBC is exported to the oceans each year. An analogous calculation based upon an Arctic DOC load of 34 Tg-C yr^{-1} (Holmes et al., 2012) and the DBC percentage for Arctic rivers, leads to an estimated DBC export by Arctic rivers of 3.0 ± 0.1 Tg-C yr^{-1}.

4.4 Refining estimates of dissolved black carbon export using CDOM

The above correlations between DOC and DBC provide a method of converting between relatively common DOC loads and rarer, more analytically challenging measurements of DBC. However, when looking for a proxy of aromatic carbon components, CDOM measurements offer even greater potential. First of all, light absorption by CDOM provides a robust empirical proxy for aromatic DOM components in Arctic rivers (Spencer et al., 2009) and model systems (Weishaar et al., 2003;Stubbins et al., 2008), including DBC concentrations in a photochemical degradation experiment (Stubbins et al., 2012). Second, measuring CDOM is simpler and cheaper than measuring DOC. Finally, estimates of CDOM can be made in situ with in water spectrophotometers (Spencer et al., 2007;Tait et al., 2015) and from space, using satellite remote sensing of water color (Griffin et al., 2011). To determine if CDOM could provide a robust proxy for DBC in Arctic rivers, a series of linear regressions were performed between DBC concentration and CDOM light absorption at wavelengths from 250 to 600 nm. Plotting the resultant correlation values (R) for the linear regressions against wavelength revealed which wavelengths provided the most robust proxies for DBC concentration (Figure 3B). Values for R peaked ($R = 0.986$) around 254 nm, a wavelength long used to estimate the relative aromatic content of DOM (Weishaar et al., 2003). At longer wavelengths, R declined gradually to 0.971 at 412 nm and 0.905 at 500 nm, before dropping more rapidly at increasing wavelengths (Figure 3B). The robust correlation at 412 nm is encouraging for those wishing to remote sense DBC from space, as estimates of CDOM at 412 nm can be retrieved from SeaWiFS (http://oceancolor.gsfc.nasa.gov/SeaWiFS) and MODIS (http://modis.gsfc.nasa.gov) satellites.

In the current study, the equation of the linear regression between DBC and CDOM light absorption at 254 nm (a_{254}) was used as a proxy to estimate DBC concentrations for each of the 410 samples analyzed for CDOM (Figure 3C). This increased the temporal extent and resolution of our DBC dataset from 25 samples over 1 year to 410 samples over 7 years. Under ice sampling for CDOM was limited as it is logistically challenging. Where data gaps exceeding one month occurred, the average under ice CDOM for each river was used to estimate winter concentrations of DBC for the modelling exercise below. This is unlikely to have significantly altered estimates of DBC export as under ice DOC concentration and water discharge are low and contribute minimally to annual Arctic river discharge and DOC loads (Holmes et al., 2012).

4.5 LOADEST model estimates of daily dissolved black carbon loads

The goal of the current study was to develop a continuous recorded of DBC export for each river across 7 years. To achieve this, daily discharge values for each river, along with the 410 CDOM derived DBC concentrations, were entered into a hydrological load estimating model (LOADEST using predefined regression model 4; http://water.usgs.gov/software/loadest) (Runkel et al., 2004) to determine daily and annual DBC loads. The predefined model 4 was chosen as it provides robust estimates of DOC export for Arctic rivers and to enable the resultant DBC loads to be compared directly to previous estimates of DOC loads made using the same model (Holmes et al., 2012). Output from the model provides estimated daily loads for DBC across the 7 years of hydrological data. To assess model performance, modelled daily loads were compared to daily loads calculated for the 25 days when DBC samples were collected. On these days, DBC loads were calculated as DBC concentration multiplied by measured discharge at the gauging station (Table S1). The hydrograph together with predicted and measured DBC loads for the Lena River are presented in Figure 4. Visual inspection indicates the model matches calculated data. Considering data for all rivers, the mean absolute error between modelled and calculated DBC loads was 11%. A two component linear regression ($R^2 = 0.987$; $p < 0.0001$) of modelled versus calculated DBC loads yielded a slope of 0.999 ± 0.02 ($p < 0.0001$) and intercept of 0.11 ± 0.11 ($p = 0.3489$). The intercept was insignificantly different from zero. Forcing the slope through zero yielded a slope of 1.01 ± 0.02 ($R^2 = 0.987$; $p < 0.0001$; Figure 5). That the slope of the regression was insignificantly different from unity (i.e. 1) indicates that use of *a*254 as a proxy for DBC and the assumptions of the LOADEST model provided a quantitatively robust estimate of daily DBC loads.

Gauging stations were near the mouths of the rivers, capturing from 82 to 100 % of each individual river's discharge, and 96% of the six rivers' combined discharge (Table 1). To determine DBC loads (Gg-C yr^{-1}) for the entirety of the river watersheds, the DBC yields (Gg-C km^{-2} yr^{-1}) for the gauged river areas were extrapolated to the total river area (Table 1). The same modeling exercise was repeated for each BPCA quantified. Annual export of each BPCA to the Arctic Ocean is presented in the Supplemental Information (Tables S2A-D). Below we focus upon the total DBC flux estimates.

The annual DBC load for the six rivers ranged from 1.4 million tons per year in 2004 and 2010 to 1.7 million tons per year in 2007. Interannual variations in DBC loads were greater than interannual variation in discharge, highlighting how variations in discharge amplify variations in the export of dissolved organics (compare Table 1 and Table 2). The greatest year-to-year variation was observed in the Kolyma (33% st. dev.) and the Yukon (27% st. dev.) Rivers while the Yenisey River (5% st. dev.) showed the lowest interannual variation in loads (Table 2). The majority of the trend in interannual variability in DBC loads between rivers stems from their trends in interannual variability in discharge, which is also greatest in the Kolyma (20%) and

minimal in the Yenisey River (4%) (Table 1). However, interannual variability in the Yukon River discharge was only 12%, suggesting that Yukon River DBC export is particularly sensitive to discharge variation. The average annual DBC load for the six rivers was 1.5 ± 0.1 million tons per year (Table 2). This translates to an average areal yield of 138 ± 13 kg-C km^{-2} yr^{-1}, a DBC yield similar to that determined for a tundra forest watershed in Northern Siberia (100 kg-C km^{-2} yr^{-1}) (Guggenberger et al., 2008), but more than double that of the Paraíba do Sul which drains an area of intense slash-and-burn land clearing in Brazil (Dittmar et al., 2012a).

The gauged area of the six rivers studied covered 10.9×10^6 km^2 or 53% of the pan-Arctic watershed (Figure 1). A pan-Arctic DBC load of 2.8 ± 0.25 million tons per year was estimated assuming DBC yields to be the same in the sampled and unsampled fractions of the pan-Arctic watershed. Riverine export of particulate BC has been presented for the six rivers studied here (Elmquist et al., 2008) (Table 2). This estimate of particulate BC loads (Elmquist et al., 2008) was made using the chemothermic oxidation (CTO) method that over estimates BC in organic rich samples such as particulate organic matter samples (Hammes et al., 2007). Therefore, the particulate BC fluxes should be considered an upper limit or an over estimate of true loads. Despite the potential for the particulate BC to be an overestimate, the load of DBC from the six rivers is eight times that of particulate BC (Table 2). This makes riverine DBC export the largest quantified term for BC removal from the pan-Arctic watershed, suggesting that DBC export plays a major role in the Arctic storage of soil BC. This appears to be true elsewhere in the world. For instance, estimated DBC export by a tropical river in Brazil is far greater than contemporary BC production in the watershed (Dittmar et al., 2012a).

Comparing DBC export to total organic carbon fluxes reveals that DBC contributes approximately 8% of DOC export (Holmes et al., 2012), which is slightly less than the 8.9% of DOC estimated using the linear correlation between DBC and DOC (Figure 3A). This flux equates to 36% of total particulate organic carbon (POC) export from the six rivers studied (Stein and MacDonald, 2004) (Table 2). The export and burial of terrestrial POC in ocean margins is a significant long-term carbon sink (Blair and Aller, 2012). By analogy, if DBC is also locked away in the marine environment, riverine DBC export represents a translocation of refractory carbon from one store to another. If however, DBC is labile within the ocean, the once refractory carbon stored in the soil black carbon pool will re-enter the contemporary carbon cycle. As DBC is refractory in the deep ocean (Dittmar and Paeng, 2009;Ziolkowski and Druffel, 2010), yet highly labile when exposed to sunlight (Stubbins et al., 2010;Stubbins et al., 2012), the efficiency of carbon translocation from soil to ocean stores may be strongest in Arctic waters where it has been demonstrated that a significant fraction of other terrestrially derived, photo-labile aromatics survive transport to the major regions of North Atlantic Deep Water formation (Benner et al., 2005). Therefore, although Arctic rivers contribute 11% of the 26.5 million tons per year of DBC delivered to the oceans globally (Jaffé et al., 2013), their relative contribution to the global deep ocean store of DBC is potentially much higher. The Arctic rivers alone would replenish the global marine pool of DBC (>12 Pg-C) (Dittmar and Paeng, 2009) in approximately 4,300 years. This initial estimate is considerably shorter than the apparent age of DBC in the open ocean (Ziolokowski and Druffel, 2010) suggesting that Arctic river DBC export and subsequent entrainment into the abyssal ocean at points of deep water formation could provide the single most important pathway of DBC delivery to the deep ocean.

5.Conclusions

Today, the DBC mediated transfer of BC from the land to the oceans is a major term in the Arctic carbon cycle. In terms of continued research, measurement of photo-labile, but bio-refractory thermogenic DOM, i.e. DBC quantified as BPCAs, and highly bio-labile thermogenic DOM quantified via levoglucosan offer an intriguing dual tracer approach to assess the dynamics of thermogenic DOM within aquatic systems {Myers-Pigg, 2015 #2367}. Optical measurements of absorbance, including at 412 nm, a wavelength amenable to remote sensing, provide robust proxies for DBC concentrations in Arctic rivers that should enable us to resolve temporal and spatial patterns in DBC cycling. Looking to the future of the Arctic, Arctic warming is set to continue at rates exceeding global average temperature increases, leading to pronounced perturbations in the Arctic which are likely to increase the production and export of BC. Warming and associated changes to the water cycle appear to be increasing Arctic wildfire frequency (Higuera et al., 2008;Hu et al., 2010), potentially increasing BC production. Arctic soils store the largest pool of organic carbon on the planet (Gruber et al., 2004). Changing climate in the Arctic is increasing river water discharge (Peterson et al., 2002;Van Vliet et al., 2013). Increasing runoff will likely increase DBC export (Figure 2). Therefore, it is likely that the transfer of BC from Arctic soils to the deep ocean will accelerate. Measurements of CDOM light absorption for discrete water samples, using in situ spectrophotometers, or via remote sensing techniques could provide an effective way of monitoring future DBC fluxes to the Arctic, so long as periodic checks are made to test the continuing veracity of the linear regression presented here (Figure 3C). The eventual fate of exported DBC in the Arctic and global ocean will influence the sign and degree of climate-carbon cycle feedbacks. If exported DBC is effectively photo-degraded in ocean surface waters, its carbon will likely enter the atmospheric CO_2 pool. However, if exported Arctic DBC reaches areas of deep water formation around Greenland, it will be reburied, not in the soils of the Arctic, but the deep waters of the global ocean.

6.Acknowledgments

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Figure 1. Map showing the six Arctic river watersheds sampled. The red dots indicate the sampling locations. Red line indicates the boundary and the grey fill the area of the pan-Arctic Ocean watershed. Data points in all subsequent figures are colored to match the river watershed colors here.

Figure 2. Panel A: Dissolved black carbon concentrations ([DBC]) versus runoff for samples from across the hydrographs of the six Arctic rivers. Black line represents the linear regression of the data ([DBC] mg-C L^{-1} = 0.359 + 21.94 × runoff; Standard error of the intercept = 0.075; Standard error of the slope = 3.48; R^2 = 0.63; n = 25; p <0.0001). Dark grey represents extent of the prediction of fit (95% confidence limit). Light grey represents extent of prediction of prediction (95% confidence limit). **Panel B: The ratio of benzeneHEXAcarboxylic acid to benzenePENTAcarboxylic acid (B6:B5) versus runoff for samples from across the hydrographs of the six Arctic rivers.** Data points from North American rivers are faded. Black line represents the logarithmic regression of the data from the Siberian rivers (B6:B5 = 0.638 + 0.0683 ln(runoff); Standard error of the intercept = 0.033; Standard error of the slope = 0.007; R^2 = 0.84; p <0.0001; n = 18).

Figure 3. Panel A: Dissolved black carbon concentration ([DBC]) versus dissolved organic carbon concentration ([DOC]). Black line represents the linear regression of the data ([DBC] = –0.019 + 0.887 × [DOC]; Standard error of the intercept = 0.035; Standard error of the slope = 0.004; R^2 = 0.96; n = 25; p <0.0001). **Panel B: Plot of correlation coefficient (R) values for linear regressions of [DBC] versus colored dissolved organic carbon Naperian light absorption coefficients (*a*CDOM) versus wavelength. Panel C: [DBC] versus *a*CDOM at 254 nm (*a*254).** Black line represents the linear regression of the data ([DBC] = 0.104 + 0.00942 × *a*254; Standard error of the intercept = 0.028; Standard error of the slope = 0.00036; R = 0.986; R^2 = 0.968; n = 25; p <0.0001).

Figure 4. Discharge plus calculated and modeled dissolved black carbon (DBC) loads for the Lena River between 2004 and 2010. Loads calculated from measured DBC were calculated as discharge on the day DBC was sampled multiplied by the measured [DBC] (n = 5). Loads calculated based upon colored dissolved organic matter (CDOM) derived DBC were calculated discharge on the days CDOM was sampled multiplied by [DBC] estimated from CDOM absorbance and the slope of the linear regression in Figure 3C (n = 132). LOADEST modeled loads were estimated using the LOADEST load model with daily discharge and CDOM based estimates of [DBC] as input data (n = 2557).

Figure 5. LOADEST modeled dissolved black carbon (DBC) loads versus loads calculated from measured [DBC] and discharge on the day of sampling. Black line represents the zero intercept linear regression of the data. When the fit was not constrained, the intercept was not significantly different from zero (0.11 ± 0.11; p = 0.35). Therefore, the intercept was constrained to zero and the fit on the graph has the following parameters (LOADEST modeled load = Load calculated from measured [DBC] × 1.012; R^2 = 0.987; Standard error of the slope = 0.019; p <0.0001; n = 25).

Table 1. Discharge gauging stations and watershed characteristics.

River / Watershed	Kolyma	Lena	Mackenzie	Ob'	Yenisey	Yukon
Discharge gauging station	Kolymskoye	Kyusyur	Tsiigehtchic	Salekhard	Igarka	Pilot Station
Area (10^6 km^2) at gauged	0.53	2.43	1.68	2.99	2.4	0.83
Area (10^6 km^2) total	0.65	2.46	1.78	2.99	2.54	0.83
% Area captured	82%	99%	94%	100%	94%	100%
Discharge (km^3 year^{-1}) gauged	111	581	298	427	636	208
Discharge (km^3 year^{-1}) total	136	588	316	427	673	208
Interannual variation in discharge (St. Dev.)	20%	9%	10%	15%	4%	12%
Runoff (mm year^{-1})	166	240	177	143	259	248

Table 2. Average dissolved black carbon (DBC) loads, yields and interannual variation in both for the six rivers studied and for the pan-Arctic watershed, plus literature values for the rivers' dissolved organic carbon (DOC) (Holmes et al., 2012), particulate organic carbon (POC) (Stein and MacDonald, 2004) and particulate black carbon (PBC) (Elmquist et al., 2008) loads.

River / Watershed	DBC load (Gg-C yr^{-1})	DBC yield (kg-C km^{-2} yr^{-1})	Interannual variation (St. Dev.)	DOC load (Gg-C yr^{-1})	PBC load (Gg-C yr^{-1})	POC load (Gg-C yr^{-1})
Kolyma	62±20	116±38	33%	818	24	310
Lena	550±68	226±28	16%	5,681	36	1,200
Mackenzie	129±20	77±12	12%	1,377	99	2,100
Ob'	262±44	87±15	17%	4,119	18	360
Yenisey	402±19	167±8	5%	4,645	10	170
Yukon	102±28	123±34	27%	1,472	1.1	12
Total for six rivers	1,506±133	138±13	-	18,109	188	4,152
Pan-Arctic	2,842±250	-	-	34,042	-	-

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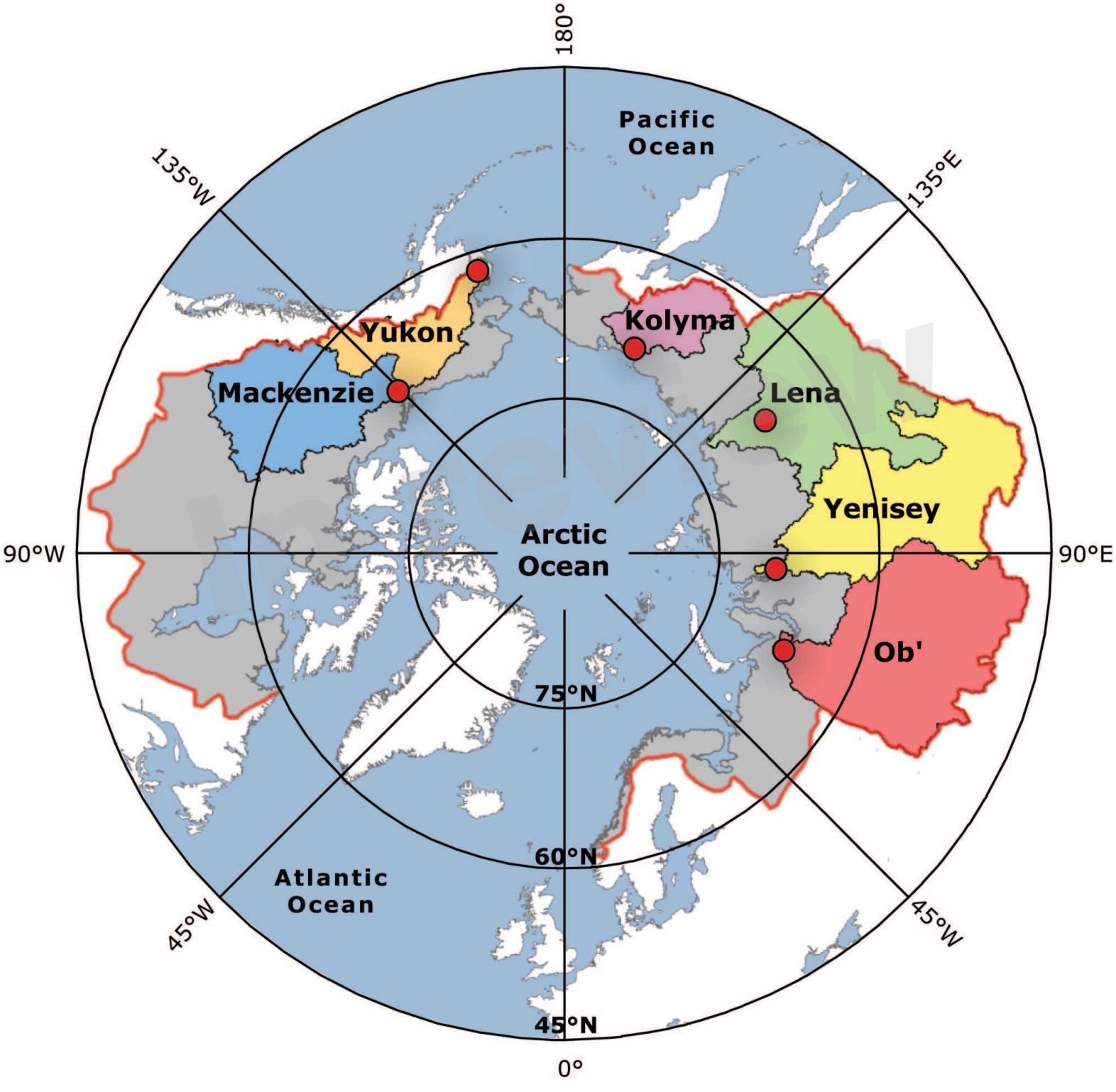
Figure 1.JPEG



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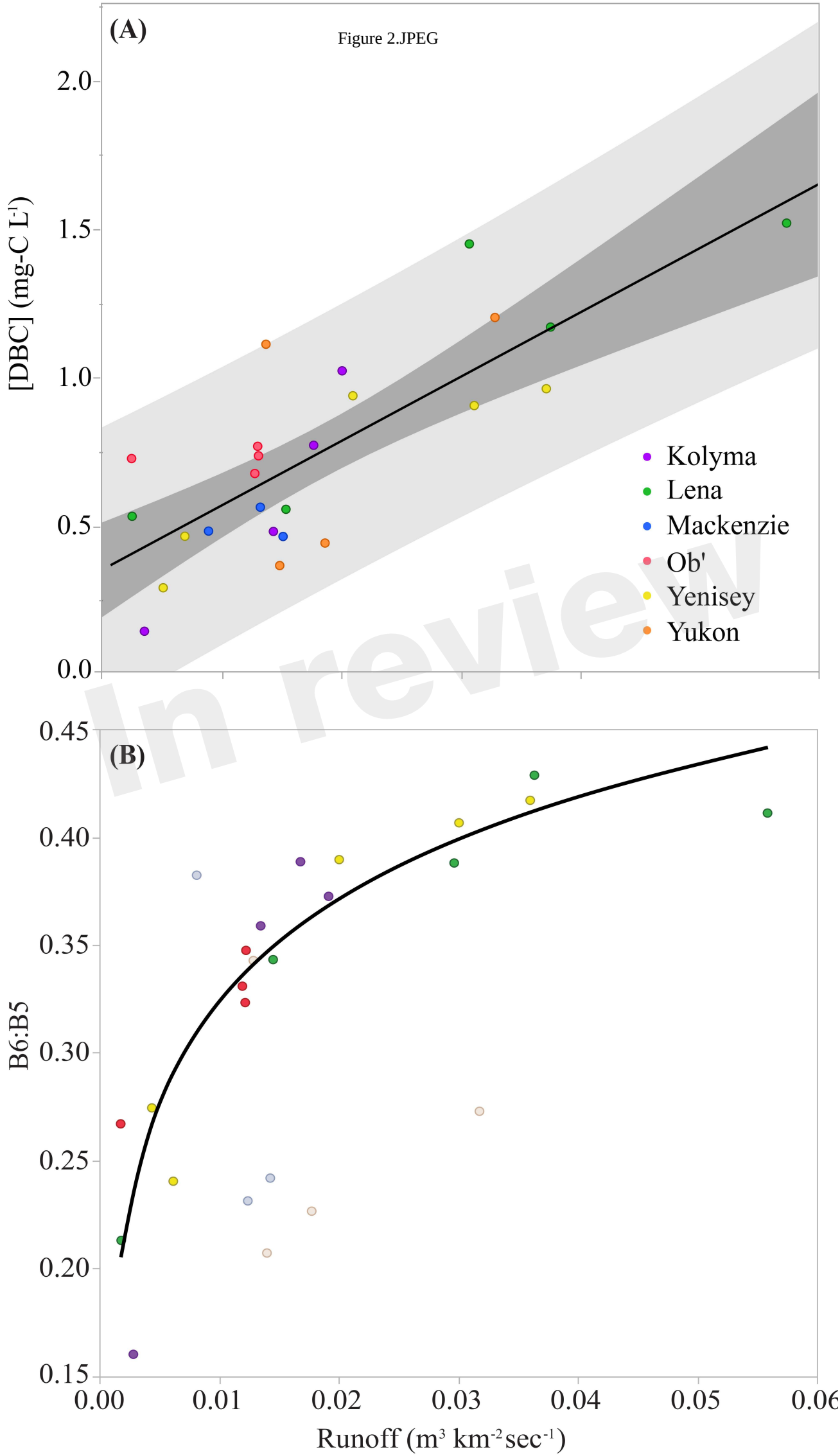

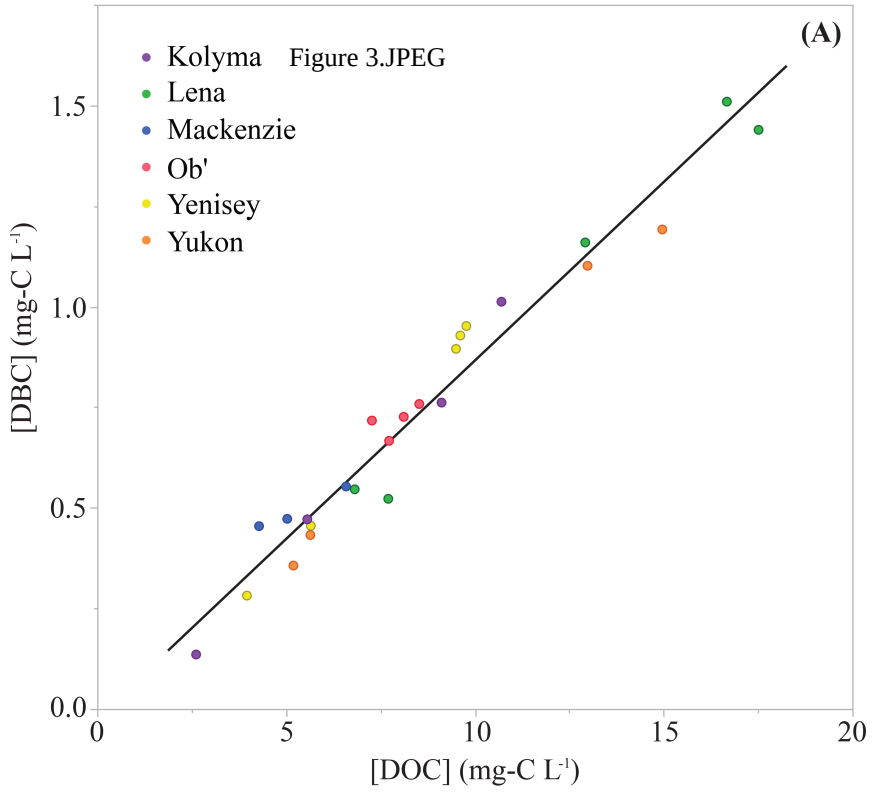

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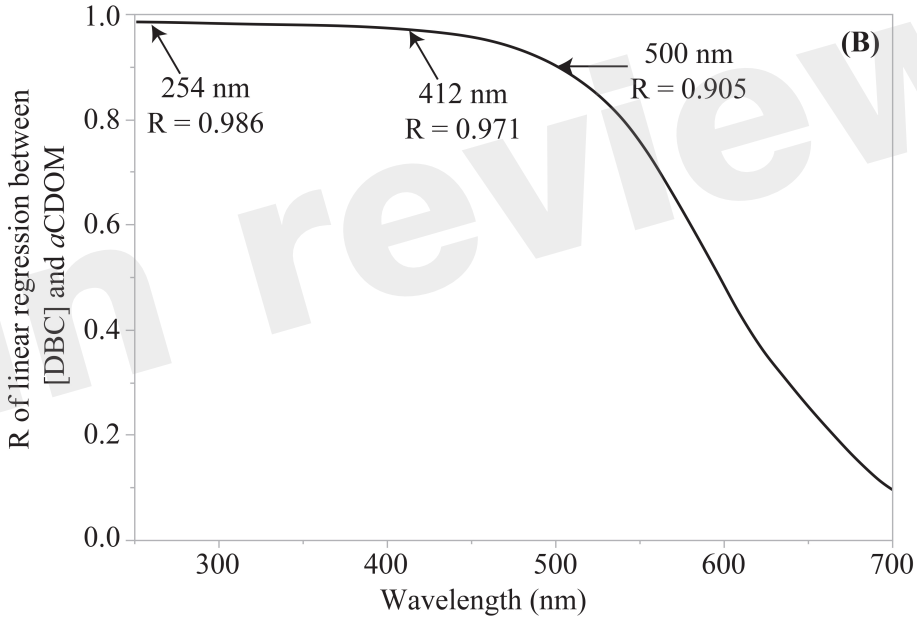

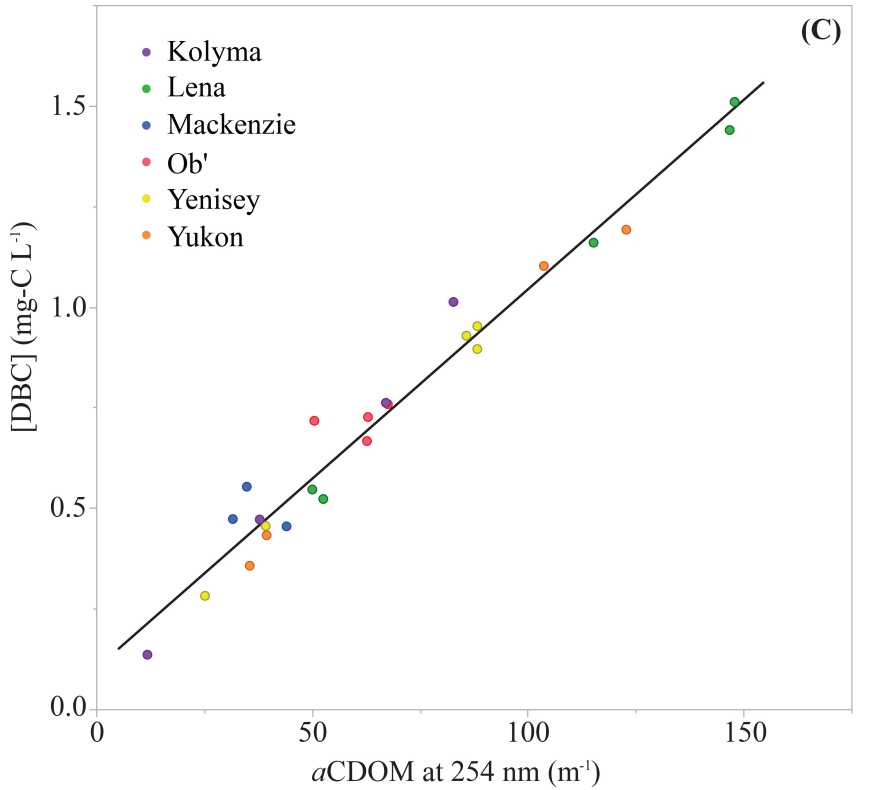

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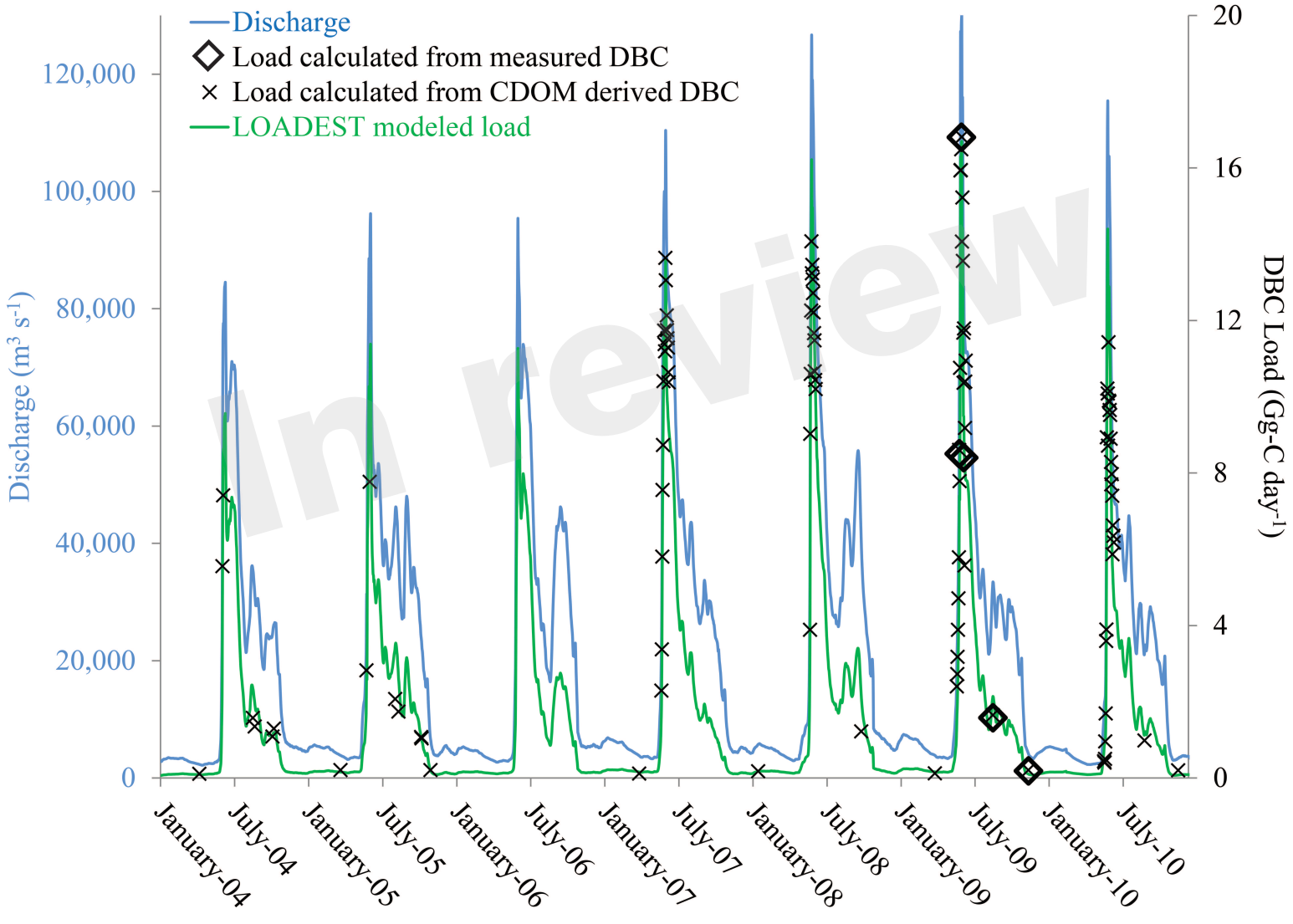

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