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A synthesis of light absorption properties of the Pan-Arctic Ocean: application to semi-analytical estimates of dissolved organic carbon concentrations from space

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Abstract

The light absorption coefficients of particulate and dissolved materials are the main factors determining the light propagation of the visible part of the spectrum and are, thus, important for developing ocean color algorithms. While these absorption properties have recently been documented by a few studies for the Arctic Ocean (e.g., Matsuoka et al., 2007, 2011; Ben Mustapha et al., 2012), the datasets used in the literature were sparse and individually insufficient to draw a general view of the basin-wide spatial and temporal variations in absorption. To achieve such a task, we built a large absorption database at the pan-Arctic scale by pooling the majority of published datasets and merging new datasets. Our results showed that the total non-water absorption coefficients measured in the Eastern Arctic Ocean (EAO; Siberian side) are significantly higher than in the Western Arctic Ocean (WAO; North American side). This higher absorption is explained by higher concentration of colored dissolved organic matter (CDOM) in watersheds on the Siberian side, which contains a large amount of dissolved organic carbon (DOC) compared to waters off North America. In contrast, the relationship between the phytoplankton absorption ($a_\phi(\lambda)$) and chlorophyll *a* (chl *a*) concentration in the EAO was not significantly different from that in the WAO. Because our semi-analytical CDOM absorption algorithm is based on chl *a*-specific $a_\phi(\lambda)$ values (Matsuoka et al., 2013), this result indirectly suggests that CDOM absorption can be appropriately derived not only for the WAO but also for the EAO using ocean color data. Derived CDOM absorption values were reasonable compared to in situ measurements. By combining this algorithm with empirical DOC vs. CDOM relationships, a semi-analytical algorithm for estimating DOC concentrations for coastal waters at the Pan-Arctic scale is presented and applied to satellite ocean color data.

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1 Introduction

The Arctic Ocean faces dramatic changes in physical environments driven by ongoing global warming. Decreases in both sea ice extent and thickness (Comiso et al., 2008; Kwok, 2007; Stroeve et al., 2008) facilitates the propagation of light into the water column, creating favorable conditions for phytoplankton photosynthetic processes when nutrients are available in the upper layer of the water column(e.g., Ardyna et al., 2013). Recent papers showed that an increase in primary production (PP) is significantly and positively correlated with open water area (Arrigo and van Dijken, 2011), suggesting that autochthonous dissolved organic carbon (DOC) resulting from the increased PP could be a non-negligible source for open waters (Wheeler et al., 1996). More importantly, in terms of the DOC budget, DOC concentrations in coastal waters are much higher than for open waters (Benner et al., 2005; Stedmon et al., 2011; Amon et al., 2012; Matsuoka et al., 2012). In addition to autotrophic sources, it is expected that recent increases in river discharges modify (Stedmon et al., 2011): (1) the total amount of DOC discharged to the Arctic Ocean, (2) the seasonality of the riverine export by increasing the flux of DOC during the base flow period (November to May), when material is older, more bio-refractory and could be transported far in the Arctic Ocean under the ice cover in winter, (3) the relative contribution of the large Arctic rivers (e.g., Lena vs. Yenisei) with consequences on DOC distribution in the Arctic Ocean. However, a comprehensive method for quantifying and continuously monitoring DOC concentrations, which takes into account their temporal and geographical variability at the Pan-Arctic scale, is presently not available.

One of the best approaches to achieve this task is to apply a semi-analytical algorithm to satellite ocean color data. Such an algorithm was recently developed for southern Beaufort Sea (Mackenzie Shelf area) waters in the Canadian Arctic (Matsuoka et al., 2013). The accuracy in the estimates of DOC concentrations using this approach relies upon an accurate retrieval of absorption coefficients of colored dissolved organic matter, CDOM at 443 nm ($a_{CDOM}(443)$, m^{-1}), and on the robustness

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of the relationship between DOC and $a_{CDOM}(443)$. The CDOM algorithm of Matsuoka et al. (2013) is based on a parameterization of absorption properties. To determine whether this algorithm can be applied to regions of the Arctic Ocean other than the Mackenzie Shelf area, the geographical variability of those optical properties must be determined.

The main objective of the present study is therefore to examine absorption properties at the Pan-Arctic scale. Based on these results, a semi-analytical algorithm for estimating DOC concentrations in coastal waters at the Pan-Arctic scale is presented and applied to satellite ocean color data.

2 Datasets and methods

2.1 In situ measurements

To provide a general overview of absorption properties, we built a large absorption database at the Pan-Arctic scale by pooling the majority of published data (Fig. 1; Table 1). In the Western Arctic Ocean (WAO), data were collected during the following five cruises during spring to autumn: the Western Arctic Shelf Basin Interaction, SBI (1) spring and (2) summer cruises aboard the *USCGS Healy* (referred to as SBI spr: 5 May to 15 June 2002, and SBI sum: 16 July to 26 August 2002, respectively), (3) the Japanese Arctic cruise aboard R/V *Mirai* (referred to as MR: 1 September to 13 October 2004), (4) the Canadian Arctic Shelf Exchange Study (CASES) cruise aboard *CCGS Amundsen* (referred to as CASES: 16 May to 2 August 2004), and (5) the MALINA cruise aboard *CCGS Amundsen* (referred to as MALINA: 30 July to 27 August 2009). In the Eastern Arctic Ocean (EAO), data were collected during the NABOS cruise aboard R/V *Viktor Buynitsky* (referred to as NABOS: 14 September to 30 September 2007). To minimize geographic bias due to a large number of data in the Chukchi and western part of the southern Beaufort Seas, absorption datasets from ICESCAPE2010 and ICECAPE2011 cruises (referred to as ICESCAPE1: 15 June to

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22 July 2010, and ICESCAPE2: 25 June to 29 July 2011, respectively) were not used for our main results. Instead, these independent datasets were used for evaluating the Bricaud and Stramski (1990) method (see Appendix A2). Radiometric data obtained from MALINA, ICESCAPE1, and ICESCAPE2 were used for evaluating a semi-analytical CDOM algorithm developed by Matsuoka et al. (2013) (see Sects. 2.2 to 2.4 for details).

Discrete water samples were collected using Niskin bottles, except at the surface where a clean container was used during the MR cruise. During the six cruises, 30, 29, 51, 94, 37, and 57 stations (SBI spr, SBI sum, MR, CASES, MALINA, and NABOS, respectively) were visited to collect water samples for pigment and absorption analyses within the euphotic zone (i.e., between the surface and the euphotic depth, z_{eu}, defined as the depth of penetration of 1 % of the surface photosynthetically available radiation (PAR)). Absorption coefficients of particles ($a_p(\lambda)$, m^{-1}) retained on GF/F filters were determined from 350 to 750 nm using a MPS-2400 spectrophotometer (Shimazu Corp.) for SBI spr, SBI sum, and MR, and a Lambda 19 (Perkin-Elmer) for CASES, NABOS, and MALINA. Because two spectrophotometers with different geometries were used for absorption measurements, the corresponding and appropriate pathlength amplification effect caused by highly scattering GF/F filter, known as the β-factor (Mitchell and Kiefer, 1988), was taken into account for each instrument (see Table 1 for details).

Phytoplankton pigments retained on the filters were extracted using methanol (Kishino et al., 1985). Absorption coefficients of non-algal particles, NAP ($a_{NAP}(\lambda)$, m^{-1}) were determined on the bleached filter. Phytoplankton absorption coefficients ($a_\phi(\lambda)$, m^{-1}) were finally obtained by subtracting $a_{NAP}(\lambda)$ from $a_p(\lambda)$. For the NABOS cruise, only $a_p(\lambda)$ data were available. To obtain $a_\phi(\lambda)$ and $a_{NAP}(\lambda)$, a numerical decomposition method proposed by Bricaud and Stramski (1990) was applied to this dataset. An evaluation of this method for Arctic samples is presented in Appendix A2. All absorption measurements were made following the NASA Ocean Optics Protocols (Mitchell et al., 2003) except MALINA data, for which we followed Rottgers and Gehnke (2012). Spectral slopes of NAP, S_{NAP} (nm^{-1}) were calculated by fitting a nonlinear model to the

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data from 380 to 730 nm, excluding the 400–480 and 620–710 nm ranges to avoid any residual pigment absorption (Babin et al., 2003).

For the CDOM absorption measurements, water samples were filtered using 0.2 µm pore-size filters immediately after sampling (see details for sample preparation in Mitchell et al., 2003; Matsuoka et al., 2012). Absorption coefficients of CDOM ($a_{CDOM}(\lambda)$, m^{-1}) were determined from 280 to 700 nm using a MPS2400 spectrophotometer (Shimazu corp.) for SBI spr, SBI sum, and MR. For CASES cruise, the filtrates were frozen at −20 °C and shipped to the laboratory at Rimouski. $a_{CDOM}(\lambda)$ spectra were then measured using a Lambda 35 (Perkin-Elmer) from 250 to 800 nm. Both spectrophotometers were equipped with 10 cm quartz cells (Bélanger et al., 2006; Matsuoka et al., 2011). For the MALINA cruise, an UltraPath liquid waveguide system was used (World Precision Instruments, Inc.), and $a_{CDOM}(\lambda)$ was obtained from 200 to 735 nm (Matsuoka et al., 2012). For the NABOS cruise, $a_{CDOM}(\lambda)$ was obtained at 412, 443, 488, 510, 532, 555, 630, 676, and 715 nm using a ac-9 (WETLabs) with 0.2 µm inline filter (Pegau et al., 2003). Spectral slopes of CDOM absorption (S_{CDOM}, nm^{-1}) were calculated by fitting a nonlinear model to the data from 350 to 500 nm, except for the NABOS cruise, for which S_{CDOM} was calculated using $a_{CDOM}(\lambda)$ at 412, 440, 488, and 510 nm. The total non-water absorption coefficient, $a_{tw}(\lambda)$ was calculated as the sum of $a_{\phi}(\lambda)$, $a_{NAP}(\lambda)$, and $a_{CDOM}(\lambda)$.

Chl *a* concentrations were determined using either fluorometric methods (chl a^{fluo}: Holm-Hansen et al., 1965; Suzuki and Ishimaru, 1990), high performance liquid chromatography (HPLC) (chl a^{HPLC}: Ras et al., 2008), or both. Comparison between chl a^{fluo} and chl a^{HPLC} showed reasonable agreement ($r^2 = 0.89$, intercept = 0.11, slope = 0.98, $N = 177$; see Appendix A1). In this study, chl a^{HPLC} was used if available. Otherwise, chl a^{fluo} was used.

The detailed method for measuring concentrations of suspended particulate matter (SPM) is documented in Doxaran et al. (2012). Briefly, 0.2 to 6 L of seawater was filtered on a pre-combusted and pre-weighted GF/F filter. After filtration of seawater, filters were systematically rinsed with 0.2 to 0.6 L of Milli-Q water to remove sea salt. The reason for

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rinsing using Milli-Q water instead of ammonium formate solution proposed by ICES (2004) is that the latter product may leave carbon deposits on the filters. This would have contaminated the CHN analyses, also made on the SPM filters to determine their particulate carbon content (see Doxaran et al., 2012). Concentration of SPM was then calculated as the difference in weight before and after filtration divided by the volume of the sample (in g m^{-3}). The SPM concentrations were measured for CASE, NABOS, and MALINA cruises.

2.2 Calculation of remote sensing reflectance

In-water upwelled radiance (L_u, $\mu W cm^{-2} nm^{-1} sr^{-1}$) and downward irradiance (E_d, $\mu W cm^{-2} nm^{-1}$) were obtained at 19 wavelengths spanning from 320 to 780 nm following the NASA Ocean Optics Protocols (Mueller and Austin, 1995) and Hooker et al. (2013). Briefly, a compact-optical profiling system (C-OPS, Biospherical Instruments Inc.) (Morrow et al., 2010) was deployed at 36 and 19 stations for MALINA and ICESCAPE1 cruises, respectively. For the ICESCAPE2 cruise, a profiling reflectance radiometer series 800 (PRR-800, Biospherical Instruments Inc.) was deployed at 24 stations. In the present study, the independent datasets from these cruises were used to evaluate our semi-analytical algorithm for deriving CDOM absorption developed by Matsuoka et al. (2013). The above-water global solar irradiance (E_s) measurements were used to correct the E_d and L_u data for change in the incident light field during water column profiling. The in-water measurements were made far away from the main ship body to minimize platform pertubations, and the above-water solar irradiance measurements were made to avoid superstructure shadows and reflections. The tilt angles were always less than 5°, as recommended by the NASA Ocean Optics Protocols (Mueller and Austin, 1995). Subsurface L_u at null depth (i.e., $L_u(0^-, \lambda)$) were obtained from the slope and intercept given by the least-squares linear regression of the log-transformed upwelled radiance vs. z. The principal data product used here is the remote sensing reflectance, $R_{rs}(\lambda) = 0.54\, L_u\,(0^-, \lambda)/E_s\,(\lambda)$, where λ indicates wavelength. In this study, $R_{rs}(\lambda)$ at six wavelengths (i.e, 412, 443, 490, 532, 555, and 670 nm corresponding ap-

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proximately to Moderate-Resolution Imaging Spectroradiometer, MODIS ocean color bands) were used to derive $a_{CDOM}(\lambda)$ at 443 nm values based on a method explained in Sect. 2.4 (Matsuoka et al., 2013).

2.3 Ocean color data

Monthly averaged climatology data over the 2002 to 2012 period for $R_{rs}(\lambda)$ at 412, 443, 488, 531, 555, and 670 nm, obtained from the MODIS Aqua ocean color sensor (http://oceandata.sci.gsfc.nasa.gov/MODISA/Binned/Monthly_Climatology/), were used in this study. A semi-analytical algorithm for deriving $a_{CDOM}(443)$ based on the method detailed in Sect. 2.4 (Matsuoka et al., 2013) was then applied to the $R_{rs}(\lambda)$ data. DOC concentrations in coastal waters were estimated using the relationships between DOC and $a_{CDOM}(443)$ as shown in Sect. 2.4.

2.4 Semi-analytical algorithms for deriving CDOM absorption and DOC concentration

A detailed description of our semi-analytical CDOM absorption algorithm is given in Matsuoka et al. (2013). Briefly, this algorithm produces $a_{CDOM}(443)$ using $R_{rs}(\lambda)$ at six wavelengths in the visible spectral domain corresponding to ocean color sensors (e.g., MODIS and MEdium Resolution Imaging Spectrometer, MERIS) by minimizing the difference between measured $R_{rs}(\lambda)$ and $R_{rs}(\lambda)$ calculated using absorption and backscattering coefficients, as in the Garver–Siegel–Maritorena (GSM) algorithm (Garver and Siegel, 1997; Maritorena et al., 2002). The following modifications were included: (1) chl *a*-specific absorption coefficients of phytoplankton for Arctic waters (Matsuoka et al., 2011) were used; (2) spectral slopes of CDM absorption, S_{CDM} (nm^{-1}) and of backscattering of particles ($b_{bp}(\lambda)$, m^{-1}), η (dimensionless) were set either to be constants or as functions of $R_{rs}(\lambda)$ (those parameters were determined based on a sensitivity analysis following Matsuoka et al., 2013); (3) $b_{bp}(555)$ was calculated using $b_{bp}(443)$ and η; (4) $a_{NAP}(443)$ was calculated using the empirical relationship between

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$a_{NAP}(443)$ and $b_{bp}(555)$ obtained for Arctic waters (i.e., $a_{NAP}(443) = b_{bp}(555)/0.2393$; Matsuoka et al., 2007); and (5) $a_{CDOM}(443)$ was obtained by subtracting $a_{NAP}(443)$ from $a_{CDM}(443)$. To estimate DOC concentrations in the near-surface coastal waters using ocean color data, a relationship between DOC and $a_{CDOM}(\lambda)$ needs to be established. Walker et al. (2013) recently showed a consistent relationship between DOC and CDOM absorption coefficient at 350 nm ($a_{CDOM}(350)$, m^{-1}) for waters at the mouth of the five major Arctic rivers (i.e., Lena, Yenisei, Ob, Mackenzie and Kolyma rivers; $DOC = 245 + 171 \cdot a_{CDOM}(443)$). The latter DOC vs. $a_{CDOM}(443)$ relationship was obtained by assuming a S_{CDOM} of 0.0175 nm^{-1} calculated using data from 350 to 600 nm in the EAO, as reported by Aas et al. (2002), to convert $a_{CDOM}(350)$ to $a_{CDOM}(443)$. Stedmon et al. (2011) reported a lower S_{CDOM} (0.0167 nm^{-1}) using the data from 300 to 650 nm. While the use of a different data range for calculating a spectral slope makes it difficult to compare results (Twardowski et al., 2004), the spectral slope reported by Stedmon et al. (2011) would not be significantly different from the one by Aas et al. (2002) if the same data range is used. In any case, the choice of a spectral slope resulted in a change of only 7 % for the slope of the DOC vs. $a_{CDOM}(443)$ relationship, which did not influence our results.

In the relationship converted in this study ($DOC = 245 + 171 \cdot a_{CDOM}(443)$), the intercept is too high for the mouth of the Mackenzie river (245 µM) in the WAO, when compared to published values (55–97 µM: Osburn et al., 2009; Matsuoka et al., 2012). The high intercept may be due to a lower DOC to $a_{CDOM}(443)$ ratio at high $a_{CDOM}(443)$ values (> 1.1 m^{-1}) in the EAO (see also Fig. 10). Thus, for the WAO, we used the relationship recently obtained by Matsuoka et al. (2012) (i.e., DOC (µM) $= 55 + 357 \cdot a_{CDOM}(443)$). These two regressions were used to estimate DOC concentrations from space using $a_{CDOM}(443)$ derived from ocean color data.

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2.5 Statistical analyses

Bio-optical quantities are often log-normally distributed in natural environments (Campbell, 1995). The normality of distribution for chl a, $a_\phi(\lambda)$, $a_{\mathrm{CDOM}}(\lambda)$ and $a_{\mathrm{NAP}}(\lambda)$ values was verified for Arctic waters using a Kolmogorov–Smirnov test (Matsuoka et al., 2011). Geometric mean and geometric SD were thus obtained for these variables in this study. Otherwise, arithmetic mean and SD were used.

3 Results and discussion

3.1 Absorption budget

In view of ocean color applications at the pan-Arctic scale, the total non-water absorption properties were examined first. We found that $a_{\mathrm{tw}}(443)$ in coastal waters (i.e., CASES, NABOS, and MALINA) tended to be higher than in oceanic waters (i.e., SBI spr, SBI sum, and MR) (Fig. 2). This result is consistent with the fact that river discharge largely influences absorption properties for the southern Beaufort and Siberian Seas, but not for the Chukchi Sea and the western part of the Beaufort Sea (Matsuoka et al., 2011, 2012; Amon et al., 2012). Over the Siberian shelves (or EAO), $a_{\mathrm{tw}}(443)$ was significantly higher ($p < 0.001$) than in the southern Beaufort Sea (or WAO) (Fig. 2; Table 1), which was also indirectly shown by Aas et al. (2002) using spectral diffuse attenuation coefficients of downwelling irradiance, ($K_{\mathrm{d}}(\lambda)$, m^{-1}) (the total non-water absorption was not directly measured in their work).

The higher $a_{\mathrm{CDOM}}(443)$ of the EAO was partly responsible for the higher $a_{\mathrm{tw}}(443)$ compared to WAO (relative contribution to $a_{\mathrm{tw}}(443)$ of 85 ± 7 % and 67 ± 19 %, respectively; Table 1 and Fig. 3). This is also consistent with the fact that the load of DOC and CDOM in the Siberian rivers (e.g., Lena, Yenisei, and Ob) is significantly higher than the Mackenzie river (Stedmon et al., 2011). CDOM absorption is strongly correlated with DOC concentrations in coastal waters of the Arctic Ocean (Matsuoka et al., 2012;

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Walker et al., 2013). The higher CDOM absorption in the EAO likely reflects higher DOC concentrations in high latitude watersheds of Siberia compared to those in North America (Raymond et al., 2007). This topic is further discussed in the Sect. 3.4.

The strong contribution of CDOM absorption is consistent with the fact that the Arctic Ocean receives the largest amount of freshwater relative to its volume (11 % of global freshwater input while its volume is only 1 % of the global ocean, Siklomanov, 1993). While this high contribution of CDOM absorption is well acknowledged especially for the WAO in both coastal and offshore waters (Bélanger et al., 2006, 2013; Matsuoka et al., 2007, 2009, 2011), it is evidenced as well here for the EAO (Fig. 4), confirming the characteristic for the whole Arctic region (68 ± 19 %, $N = 603$; Table 1). Consequently, waters include high proportion of CDOM for both oceanic and coastal waters at the Pan-Arctic scale, significantly influencing several estimates such as $K_d(\lambda)$ and primary production (PP) as derived from ocean color data (Reynolds et al., 2013; Arrigo et al., 2013).

3.2 Parameterization

While Matsuoka et al. (2011) examined absorption properties of the WAO, the majority of the data in that study were obtained for oceanic waters. To generalize the absorption properties for Arctic waters, large datasets of absorption in coastal waters from both the southern Beaufort and Siberian Seas were added and analyzed in this study.

To examine differences in bio-optical properties between WAO and EAO, $a_p(443)$ was plotted as a function of chl *a* (Fig. 5a). Even when the outliers, observed outside the 95 % confidence intervals, were included, $a_p(443)$ showed significant positive correlation with chl *a* ($r^2 = 0.62$, $p < 0.0001$; $N = 657$), which was quite similar to the correlation observed by Bricaud et al. (1998) at lower latitudes. High pigment packaging effect has been acknowledged as a common feature for Arctic phytoplankton absorption, resulting in lower chl *a*-specific $a_\phi(\lambda)$ ($a^*_\phi(\lambda)$,m^2 mg chl a^{-1}) values relative to those at lower latitudes (e.g., Mitchell, 1992; Matsuoka et al., 2011). Because

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particulate absorption is composed of phytoplankton and NAP absorption, higher NAP absorption values for Arctic waters compared to those at lower latitudes ($p < 0.05$; Table 2) leads to a similar $a_p(443)$ vs. chl *a* relationship. The higher NAP likely originates from materials derived from glaciers and delivered by river runoff or from coastal erosion by ice (Mitchell and Holm-Hansen, 1991; Hodgkins et al., 2003), by accumulation of organic material in sea ice due to atmospheric deposition of aerosols or by ice algae in situ production (Bélanger et al., 2013).

Figure 5b represents the relationship between a_ϕ (443) and chl *a*. Less variability in this relationship was observed compared to the $a_p(443)$ vs. chl *a* relationship. A strong correlation between the two variables was found ($r^2 = 0.78$, $p < 0.0001$; $N = 657$). As expected, this regression line at chl $a < 1.0\,\mathrm{mg\,m^{-3}}$ was significantly below the one obtained by Bricaud et al. (1998) at lower latitudes, demonstrating the higher pigment packaging effect for Arctic waters.

It should be stressed that while significantly higher $a_{CDOM}(443)$ in the EAO was observed compared to WAO (Figs. 3 and 4), the a_ϕ (443) vs. chl *a* relationships between the EAO (or NABOS dataset) and WAO (or the rest of the datasets) showed no significant difference or were statistically similar ($p = 0.35$, *F* test). Despite the geographical difference between the WAO and EAO, this result suggests that the same relationship can be applied for both. More importantly, because our semi-analytical CDOM absorption algorithm is based on chl *a*-specific $a_\phi(\lambda)$ estimates (Matsuoka et al., 2013), this result highlights that our algorithm can be applied not only for WAO but also for EAO.

Matsuoka et al. (2011) and Wang et al. (2005) showed that $a_\phi(\lambda)$ in the visible spectral domain is highly correlated with a_ϕ (443) which can be obtained using ocean color data. While a large dataset including both oceanic and coastal waters was used in this study ($N = 993$), $a_\phi(\lambda)$ showed excellent correlation with a_ϕ (443) (Fig. 6 and Table 3). This kind of statistical approach allows obtaining spectral $a_\phi(\lambda)$ values using ocean color data, which can be further used for operating a spectral primary production model from space.

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Statistics for $a_{CDOM}(443)$ and $a_{NAP}(443)$ and their spectral slopes are shown in Table 4. Results are consistent with those provided by Matsuoka et al. (2011), although much larger datasets obtained from various locations were used in the present study ($N = 859$, compared to $N = 408$ in Matsuoka et al., 2011), suggesting the ubiquitous features in waters at the Pan-Arctic Ocean.

3.3 Evaluation of the CDOM absorption algorithm

Estimates of DOC concentrations in Arctic coastal waters using ocean color data are reliable when CDOM absorption values are appropriately derived (Matsuoka et al., 2013). We evaluated the performance of a tuned semi-analytical CDOM absorption algorithm using our Arctic datasets (Fig. 7); in this study, all data from MALINA, ICESCAPE1 and ICESCAPE2 datasets were used for this evaluation, whereas Matsuoka et al. (2013) only used data from the MALINA dataset. It is important to recall that this evaluation was performed using independent datasets (e.g., MALINA, ICESCAPE1, and ICESCAPE2 datasets) that were not used for developing the algorithm (i.e., data from SBI spr, SBI sum, and MR cruises were used for this development). Results showed that the semi-analytical CDOM algorithm works reasonably well with sufficient accuracy (Table 5). On average, $a_{CDOM}(443)$ can be derived using our CDOM algorithm within 9 %. Only four data points were located above the 50 % error intervals (circles in Fig. 7). The $a_{CDOM}(443)$ estimates at these points were likely influenced by the presence of mycosporine-like amino acids (MAAs) which were apparent in $a_{\phi}(\lambda)$ spectra (see Appendix A3). Although in situ $R_{rs}(\lambda)$ data in the EAO are currently not available, this result gives confidence that $a_{CDOM}(443)$ can be derived accurately using ocean color data.

3.4 Ocean color application

Based on the evaluation of our CDOM algorithm as well as bio-optical properties as shown above, we derived $a_{CDOM}(443)$ from satellite data ($a^{sat}_{CDOM}(443)$, m^{-1}) by apply-

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ing this algorithm to MODIS climatological data (Fig. 8). To our knowledge, this is the first synoptic view of $a_{CDOM}(443)$ for the whole Arctic Ocean using a semi-analytical approach. Waters with high CDOM absorption are more widely distributed in the EAO (e.g., Laptev and Kara Seas) than in the WAO (e.g., southern Beaufort Sea). For August, geometric mean (G. Mean) and geometric standard deviation (G. SD) values of $a^{sat}_{CDOM}(443)$ in the southern Beaufort Sea (0.059 and 2.363 m^{-1}, respectively) were similar to our field observations for the MALINA cruise (0.055 and 2.265 m^{-1}, respectively) during the same time period (Matsuoka et al., 2012). G. Mean and G. SD values for $a^{sat}_{CDOM}(443)$ in the Laptev (0.138 and 2.833 m^{-1}, respectively) and Kara Seas (0.073 and 3.037 m^{-1}, respectively) are higher than those in the southern Beaufort Sea (Fig. 9). The highest $a^{sat}_{CDOM}(443)$ value observed in the Kara Sea (4.353 m^{-1}) is consistent with in situ measurements (up to 5 m^{-1}; Aas et al., 2002; Heim et al., 2013; Orek et al., 2013; Walker et al., 2013). In addition to our evaluation shown in Fig. 7, this result highlights the reliability of satellite ocean color data for Arctic waters (see also Fig. 5 in Matsuoka et al., 2013).

To estimate DOC concentrations in coastal waters using ocean color data, a DOC concentration vs. CDOM absorption relationship needs to be established. Matsuoka et al. (2012) recently showed a strong correlation between the two variables in southern Beaufort Sea waters ($r^2 = 0.97$; $p < 0.0001$). Similarly, DOC concentrations were well correlated with $a_{CDOM}(443)$ in the EAO (Walker et al., 2013). It is important to note that the DOC vs. $a_{CDOM}(443)$ relationships differ between the WAO and EAO (Fig. 10), suggesting that different relationships between DOC and $a_{CDOM}(443)$ need to be applied for EAO and WAO.

To estimate DOC concentrations in the near surface waters of the Arctic Ocean, the regression of DOC vs. $a_{CDOM}(443)$ shown in Fig. 10 was applied to $a^{sat}_{CDOM}(443)$ image. Similarly to $a^{sat}_{CDOM}(443)$ distribution, waters showing high DOC concentrations were widely distributed in the EAO compared to WAO (Fig. 11). The G. means of DOC concentrations estimated from satellite data (DOC^{sat}, µM) in the southern Beaufort

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Sea (82 µM) were of the same order of magnitude as in situ measurements for the MALINA cruise (79 µM: Matsuoka et al., 2012). The values in the Laptev (279 µM) and Kara Seas (267 µM) were higher than in the southern Beaufort Sea (Fig. 12), which is consistent with in situ measurements (Amon et al., 2012; Walker et al., 2013). The high DOC concentrations in the EAO are likely due to higher DOC concentrations in the high latitude watersheds of Siberia compared to those in North America (Raymond et al., 2007; Stedmon et al., 2011). Ongoing global warming will likely increase the release of presently sequestered carbon that originates, in part, from thawing of the permafrost (e.g., Frey and Smith, 2005; Stedmon et al., 2011). Continuous monitoring and quantification of DOC concentrations and the budget for the whole Arctic Ocean are therefore urgently required to better understand modifications in carbon cycling as a result of global warming.

4 Conclusions

This study examined light absorption properties in the Pan-Arctic Ocean using a large dataset including both oceanic and coastal waters. Our results clearly showed the specificity of those properties: high proportion of CDOM absorption, high pigment packaging effect. Despite the high proportion of CDOM absorption to the total non-water absorption, the relationship between phytoplankton absorption at 443 nm and chl *a* concentration was not significantly different between the WAO and EAO. Our semi-analytical CDOM algorithm depends on chl *a*-specific $a_{\phi}(\lambda)$ estimates, highlighting the applicability for the whole Arctic Ocean. Using DOC vs. $a_{\mathrm{CDOM}}(443)$ relationships, DOC concentrations in coastal waters can now be estimated semi-analytically using satellite ocean color data. Our statistical results demonstrated that both $a_{\mathrm{CDOM}}(443)$ values and DOC concentrations obtained using satellite ocean color data are reasonable compared to in situ measurements, suggesting its potential utility for obtaining a quantitative estimate of the carbon budget of the Arctic Ocean.

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The DOC budget of the Arctic Ocean is expected to change rapidly due to sea ice reduction, permafrost thawing, and river discharge increases as consequences of global warming. To examine this issue temporally and geographically using satellite ocean color data, we developed a semi-analytical algorithm for estimating DOC concentrations in Arctic coastal waters. Compared to empirical algorithms that have been proposed (e.g., Mannino et al., 2008; Fichot and Benner, 2011), because CDOM absorption is semi-analytically derived from ocean color data, this algorithm depends less on empirical relationships established for particular time periods and areas. Our pan-Arctic dataset and robust semi-analytical methods should improve satellite estimates of DOC concentrations in surface waters of the Arctic Ocean and help to enhance our understanding of modifications of DOC cycles in the Arctic Ocean. Further work regarding inter-annual variability in DOC budget is required.

We acknowledge that an issue regarding the seasonal variability in the relationship between DOC concentrations and CDOM absorption needs to be considered. While no study examining this issue has not yet been conducted so far for Arctic waters, Mannino et al. (2008) demonstrated in the US Middle Atlantic Bight that the intercept of the DOC vs. $a_{CDOM}(443)$ relationship changed seasonally in their study region, whereas the slope remained unchanged. This result suggests that the effect of the intercept is important when estimating DOC concentrations from space and warrants further study.

Appendix A

A1 Comparison of chl *a* determination between HPLC and fluorometric method

Chl *a* concentrations determined fluorometrically (chl a^{fluo}) were compared to those using the HPLC (chl a^{HPLC}) technique (Fig. A1). Correlation between the two quantities was high ($r^2 = 0.89$, $N = 177$), and slope was not significantly different from 1 : 1 line ($p < 0.0001$). This result suggests that in this study, chl a^{fluo} can appropriately replace chl a^{HPLC} when chl a^{HPLC} is not available.

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A2 Evaluation of estimated phytoplankton absorption using Bricaud and Stramski (1990)'s method

We evaluated the performance of the Bricaud and Stramski (1990)'s method to estimate phytoplankton absorption using total particulate absorption data from the ICESCAPE1 cruise (Fig. A2). Results showed that $a_\phi(\lambda)$ values can be derived with high accuracy using this method at wavelengths in the visible spectral domain. This method was used for the NABOS dataset.

A3 High UV absorption for some phytoplankton communities

High in phytoplankton absorption spectra around 330 nm were observed at four stations during ICESCAPE cruises. The presence of mycosporine-like amino acids (MAAs) in natural waters has been reported at all latitudes (e.g., Karsten et al., 1991, 1998; Whitehead and Vernet, 2000; Tilstone et al., 2010). The majority of MAAs absorption peaks are observed at 330–334 nm due to several types of MAAs (e.g., shinorine, Porphyra-334, Asterina; Carreto et al., 2005; Llewellyn and Airs, 2010). A clear bump was also observed at 360 nm at station 38 during ICESCAPE1, which corresponded to the peak of palythene (Llewellyn and Airs, 2010). Although actual concentrations of MAAs during our observations are not available, the strong UV absorption observed for some samples in this study suggest MAAs were present. Since MAAs are water soluble, they may be released from the cells upon freezing-melting processes of sea ice, senescence, or grazing entering the dissolved organic pool and hence contribute to our $a_{\mathrm{CDOM}}(443)$ estimates (circles in Fig. 7). It is interesting to note that $a_\phi(\lambda)$ at 330 and 360 nm can influence $R_{\mathrm{rs}}(\lambda)$ in the visible spectral domain. A similar result was also observed using an empirical relationship between $a_{\mathrm{CDOM}}(443)$ and $K_{\mathrm{d}}(380)/K_{\mathrm{d}}(780)$ (Hooker, unpublished). The strong impact of MAAs absorption and spectral reflectance in the UV spectral domain during a massive red tide was reported by Kahru and Mitchell (1998) and is the basis for the Red Tide index published for the Global Imager (GLI) algorithm (Mitchell and Kahru, 2009). This influence of MAAs on UV-Visible absorption may allow

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estimates of MAAs using ocean color data in the future if the challenge of atmospheric correction in the UV spectral domain can be solved.

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Table 1. Summary of our absorption datasets. The total non-water absorption ($a_{tw}(\lambda)$, m^{-1}), and individual contribution by phytoplankton ($a_{\phi}(\lambda)$, m^{-1}), NAP ($a_{NAP}(\lambda)$, m^{-1}), and CDOM ($a_{CDOM}(\lambda)$, m^{-1}) are shown. To obtain $a_{\phi}(\lambda)$ and $a_{NAP}(\lambda)$ values, a different β-factor was used for each instrument because of the different geometry and phytoplankton species composition (see below).

Year	Season	Cruise	$a_{tw}(443)$	$\%a_{\phi}$ (443)	$\%a_{NAP}(443)$	$\%a_{CDOM}(443)$	N	β-factor
2002	Spring	SBI spr	0.10 ± 0.04	0.27 ± 0.15	0.15 ± 0.10	0.58 ± 0.20	68	1
2002	Summer	SBI sum	0.11 ± 0.13	0.31 ± 0.14	0.16 ± 0.10	0.53 ± 0.16	107	1
2003–2004	Spring/Summer /Autumn	CASES	0.19 ± 0.20	0.16 ± 0.15	0.15 ± 0.10	0.68 ± 0.18	112	2[a]
2004	Autumn	MR	0.10 ± 0.06	0.18 ± 0.12	0.08 ± 0.05	0.74 ± 0.14	179	1
2007	Summer	NABOS	0.32 ± 0.15	0.08 ± 0.04	0.08 ± 0.04	0.85 ± 0.07	18	3[a]
2009	Summer	MALINA	0.19 ± 0.45	0.13 ± 0.09	0.15 ± 0.15	0.73 ± 0.18	119	4[b]
Average	All	All	0.14 ± 0.23	0.20 ± 0.14	0.13 ± 0.11	0.68 ± 0.19	603	–

1: Cleveland and Weidemann (1993).
2: Tassan and Ferrari (1995, 2002).
3: Bricaud and Stramski (1990); Allali et al. (1997).
4: Bélanger et al. (2013).
[a] Different β-factor was used for CASES (Tassan and Ferrari, 2002) and NABOS (Bricaud and Stramski, 1990; Allali et al., 1997) using the same Perkin-Elmer 19 spectrophotometer equipped with a 60 mm integrating sphere. During NABOS cruise (late summer to autumn), a mean value of chl *b* to chl *a* ratio of 0.15 was observed, which was similar to that obtained in the southern Beaufort Sea over the same time period (0.19) when mixture of small phytoplankton (e.g., flagellates) dominated (Matsuoka et al., 2009). This result suggests that small phytoplankton dominated in EAO waters during NABOS cruise. Bricaud and Stramski (1990) and Allali et al. (1997) obtained a β-factor for smaller type of phytoplankton species, which was applied for the NABOS dataset. For the CASES cruise, large phytoplankton such as diatoms dominated (Terrado et al., 2008). Tassan and Ferrari (1995, 2002) determined a β-factor for larger phytoplankton, which was applied to the CASES dataset.
[b] A Perkin-Elmer 19 spectrophotometer equipped with a 150 mm integrating sphere was used.

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Table 2. Average values and standard deviations of $a_{NAP}(443)$ normalized by SPM ($a_{NAP}(443)^*$,$m^2\,g^{-1}$). *N* indicates the number of samples. For comparison, values obtained for the COASTLOOC cruises in the literature (Babin et al., 2003) are also shown.

	Cruise	$a_{NAP}(443)^*$	*N*
This study	CASES	0.0360 ± 0.0275	107
	NABOS	0.0014 ± 0.0019	15
	MALINA	0.0602 ± 0.0300	121
	All	0.0459 ± 0.0324	243
	All but NABOS	0.0488 ± 0.0312	228
Babin et al. (2003)	COASTLOOC	0.0410 ± 0.0230	328

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Table 3. Correlations between $a_\phi(\lambda)$ and a_ϕ (443) in this study.

$a_\phi(\lambda)$ at wavelength	412	490	555	670	N
r^2	0.98	0.99	0.87	0.95	993

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Table 4. Statistics of $a_{CDOM}(443)$ and $a_{NAP}(443)$ at 443 nm with their spectral slopes, S_{CDOM} and S_{NAP}, respectively.

Cruise	$a_{CDOM}(443)$ Geometric mean (SD)	S_{CDOM} Arithmetic mean ±1 SD	$a_{NAP}(443)$ Geometric mean (SD)	S_{NAP} Arithmetic mean ±1 SD	*N*
SBI spr	0.0534 (2.1231)	0.0184 ± 0.0036	0.0114 (2.4180)	0.0095 ± 0.0022	80
SBI sum	0.0429 (1.7890)	0.0205 ± 0.0035	0.0115 (2.7128)	0.0102 ± 0.0015	111
MR	0.0662 (1.6732)	0.0155 ± 0.0031	0.0062 (2.1135)	0.0108 ± 0.0009	179
CASES	0.0992 (2.6003)	0.0198 ± 0.0027	0.0187 (4.3476)	0.0103 ± 0.0011	132 (173)
NABOS	0.2463 (1.8366)	0.0209 ± 0.0044	0.0141 (2.7972)	0.0165 ± 0.0062	31 (22)
MALINA	0.0559 (2.1947)	0.0185 ± 0.0013	0.0078 (4.8963)	0.0070 ± 0.0014	326 (436)
All	0.0642 (2.2577)	0.0184 ± 0.0032	0.0095 (3.9657)	0.0090 ± 0.0026	859 (1001)

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Table 5. Comparison of $a_{CDOM}(443)$ estimates ($a^{mod}_{CDOM}(443)$, m^{-1}) with in situ $a_{CDOM}(443)$ ($a^{obs}_{CDOM}(443)$, m^{-1}) using independent datasets which were not used for developing the CDOM algorithm. Data from MALINA, ICESCAPE1, and ICESCAPE2 were used. Root mean square error (RMSE) and mean normalized bias (MNB) as well as coefficient of determination (r^2), intercept, and slope are provided.

Datasets	r^2	Intercept	Slope	RMSE	MNB	N
This study	0.87	−0.022	0.97	0.069	8.58	79

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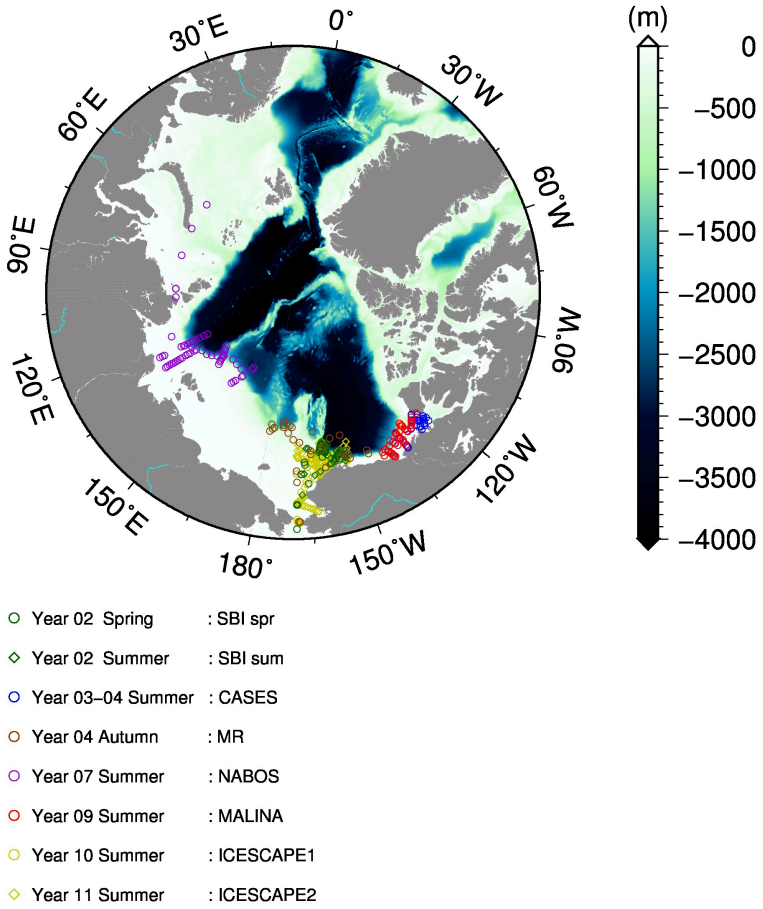

Fig. 1. Locations of sampling stations for the SBI spr (green circles), SBI sum (green diamonds), CASES (blue circles), MR aut (brown circles), NABOS (purple circles), MALINA (red circles), ICESCAPE1 (gold circles), and ICESCAPE2 (gold diamonds) in the Arctic Ocean.

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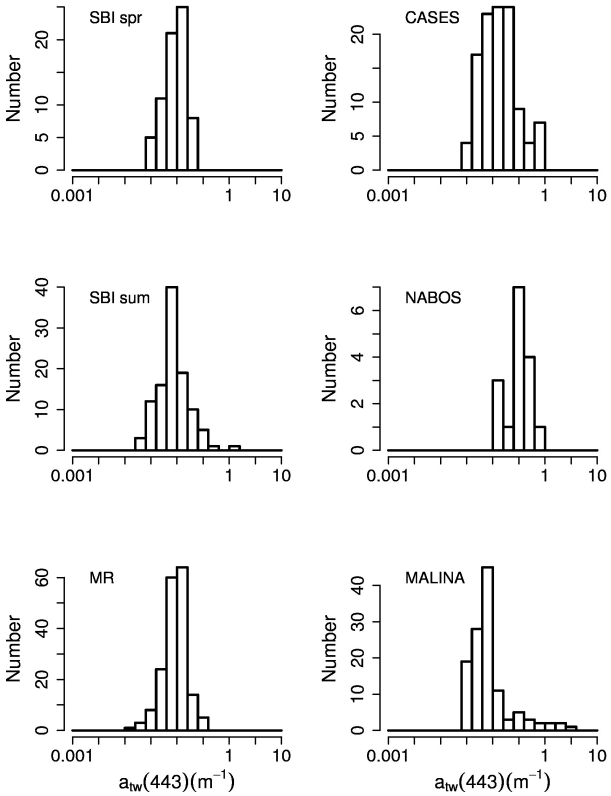

Fig. 2. Histogram of the total non-water absorption at 443 nm ($a_{tw}(443)$, m^{-1}) for SBI spr, SBI sum, MR (left) and CASES, NABOS, MALINA (right).

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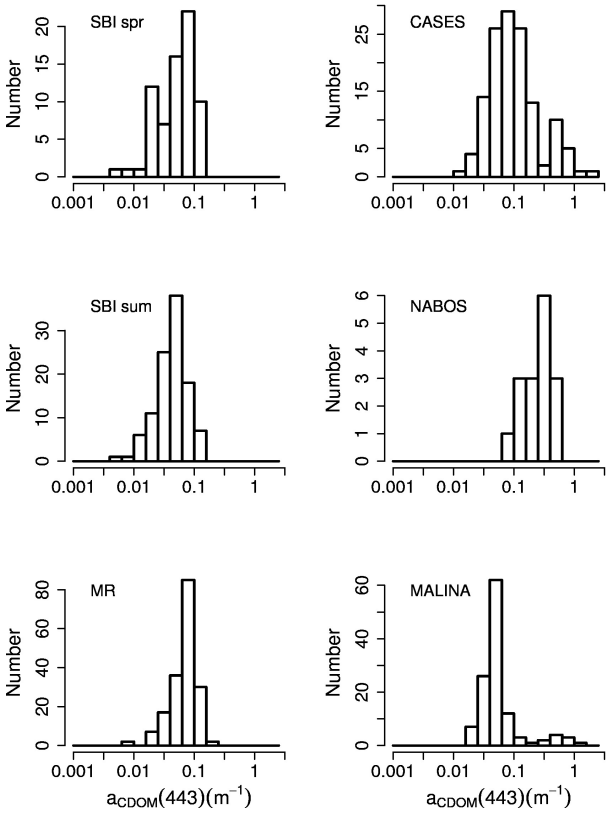

Fig. 3. Histogram of CDOM absorption at 443 nm ($a_{CDOM}(443)$, m^{-1}) for SBI spr, SBI sum, MR (left) and CASES, NABOS, MALINA (right).

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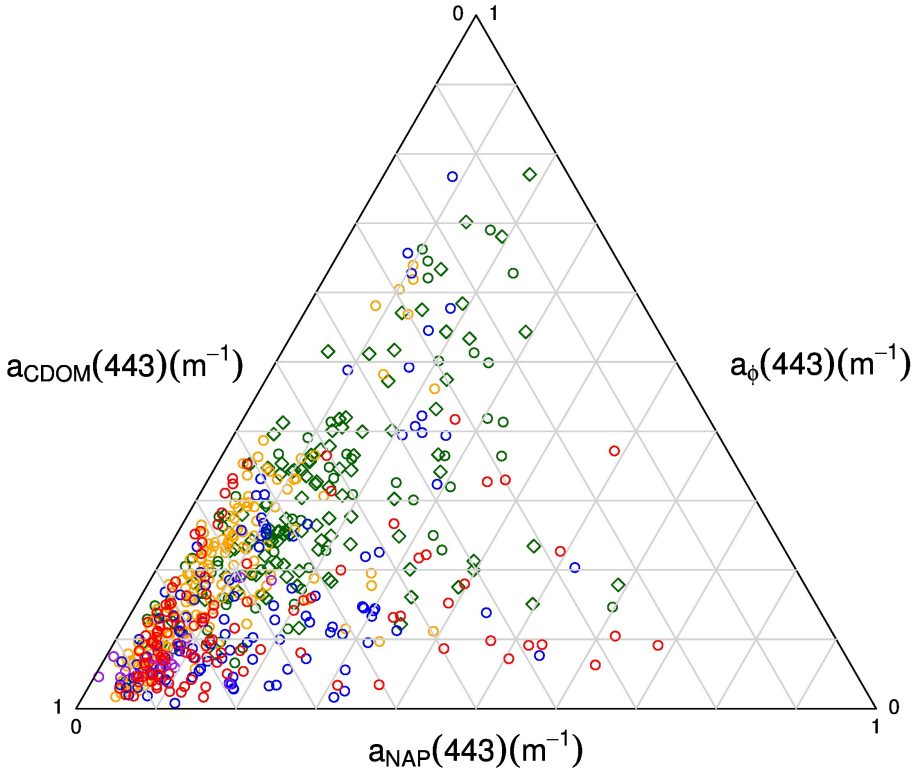

Fig. 4. The contribution of absorption coefficients of phytoplankton (a_{ϕ} (443), m^{-1}), NAP ($a_{NAP}(443)$, m^{-1}), and CDOM ($a_{CDOM}(443)$, m^{-1}) absorption coefficients to the total non-water absorption at 443 nm. See Fig. 1 for symbols.

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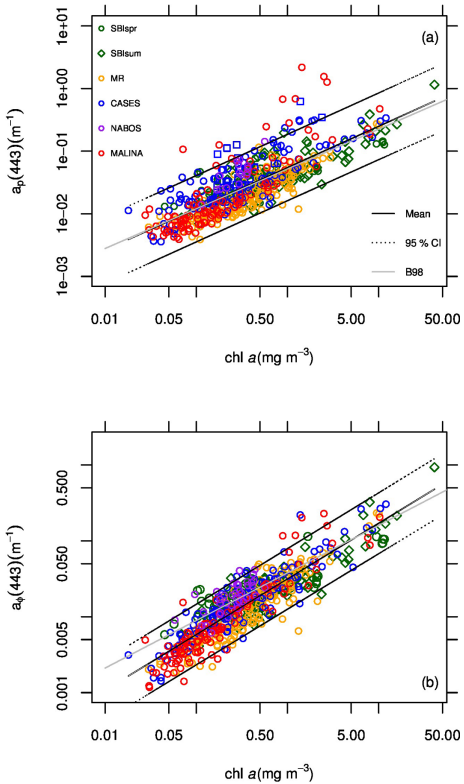

Fig. 5. (a) Relationship between the total particulate absorption coefficients at 443 nm ($a_p(443)$, m^{-1}) and chl *a* for our Arctic datasets. The regression line ($a_p(443) = 0.0548[\text{chl } a]^{0.658}$, $N = 657$; $p < 0.0001$) and ±95 % confidence intervals are displayed. The regression line obtained by Bricaud et al. (1998) (grey) is also overlaid for comparison. **(b)** Relationship between a_ϕ (443) and chl *a* (a_ϕ (443) $= 0.0315[\text{chl } a]^{0.733}$, $N = 657$; $p < 0.0001$).

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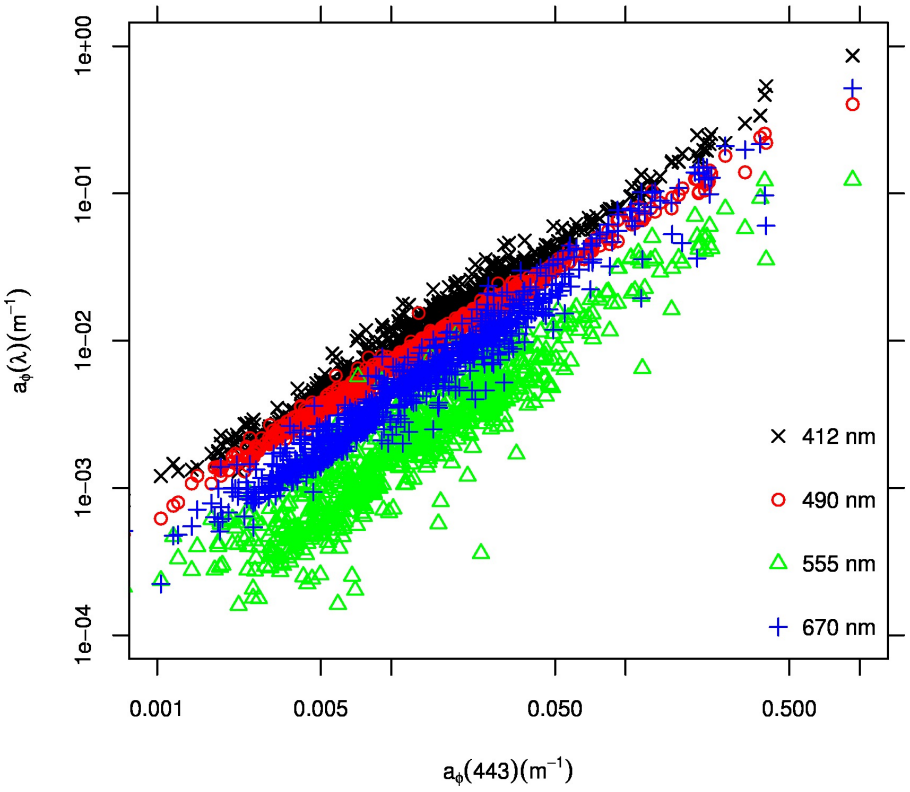

Fig. 6. Relationship between a_ϕ (443) and $a_\phi(\lambda)$ at 412, 490, 555, and 670 nm. Coefficients of determination are shown in Table 3.

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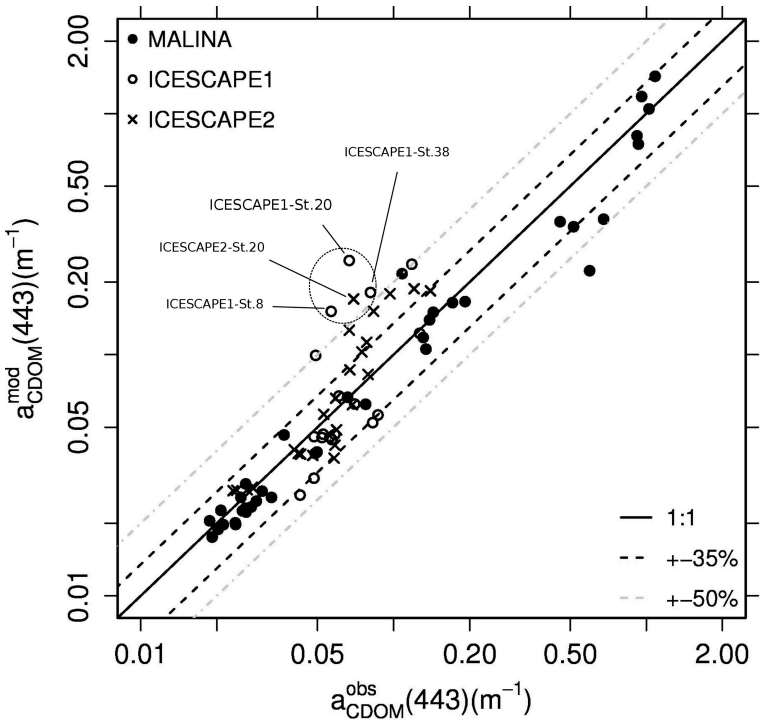

Fig. 7. A comparison of estimated CDOM absorption ($a^{mod}_{CDOM}(443)$, m^{-1}) and in situ measurements ($a^{obs}_{CDOM}(443)$, m^{-1}) using datasets (MALINA, ICESCAPE1, and ICESCAPE2) that were not used for developing our CDOM algorithm (i.e., data from SBI spr, SBI sum, and MR cruises were used for the algorithm development). Phytoplankton absorption spectra for four data points above the 50 % error are shown and explained in Fig. A3 and Appendix A3.

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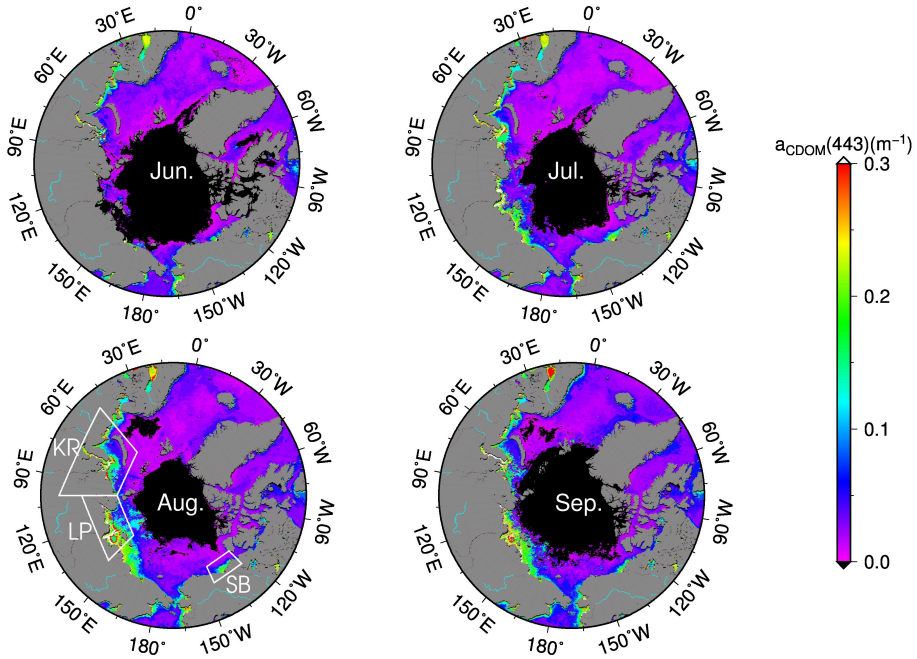

Fig. 8. Climatology of CDOM absorption at 443 nm from satellite sensors ($a^{sat}_{CDOM}(443)$, m^{-1}) from June to September, obtained by applying our CDOM absorption algorithm to MODIS monthly-averaged climatology of $R_{rs}(\lambda)$ data over the 2002–2012 period. Three areas were defined for examination of $a^{sat}_{CDOM}(443)$ values as follows: southern Beaufort (SB: 125–145° W, 68–72° N), Laptev (LP: 100–145° E, 69–77° N), and Kara seas (KR: 50–100° E, 64–77° N). Histograms of $a^{sat}_{CDOM}(443)$ values within these areas are shown in Fig. 9.

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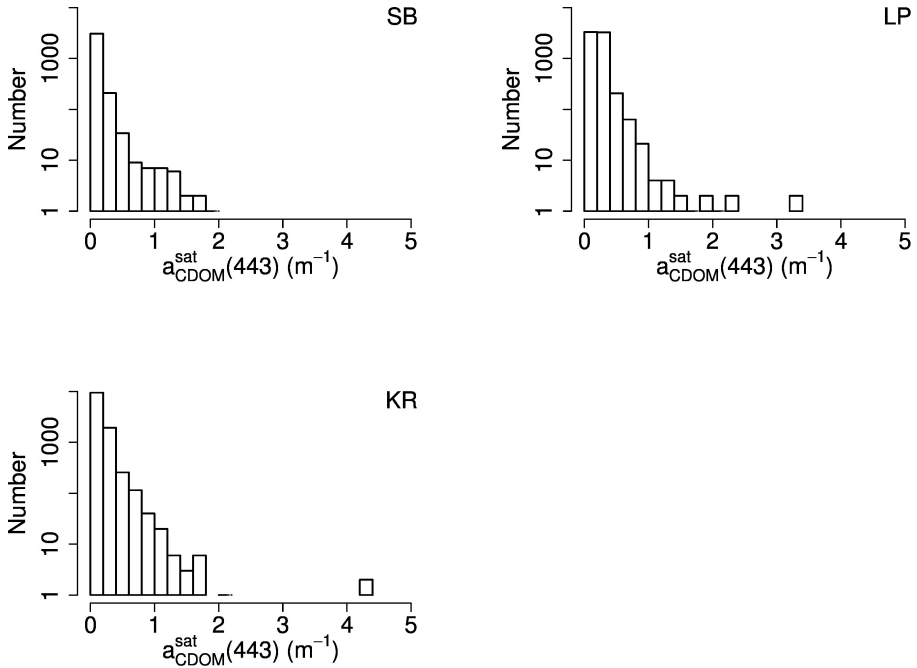

Fig. 9. Histogram of $a^{sat}_{CDOM}(443)$ values in the SB, the LP, and the KR seas defined in Fig. 8.

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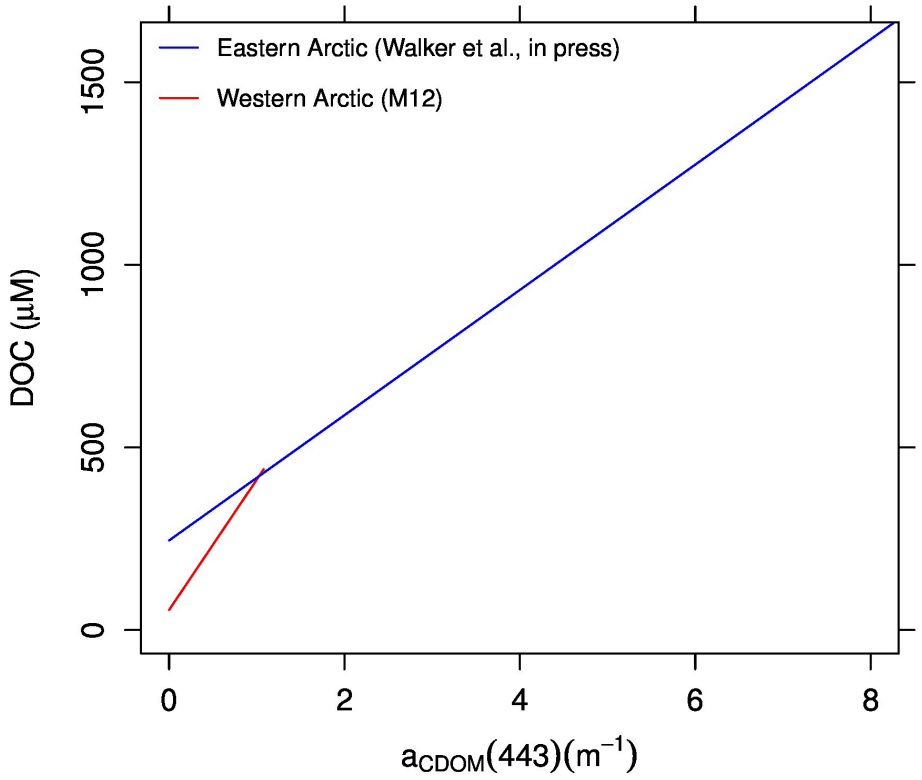

Fig. 10. In situ between DOC and $a_{CDOM}(443)$ for WAO (M12: Matsuoka et al., 2012; $r^2 = 0.97$, $p < 0.0001$; DOC = 55 + 357*$a_{CDOM}(443)$) and EAO (W13: Walker et al., in press; $r^2 = 0.90$, $p < 0.0001$; DOC = 245 + 171*$a_{CDOM}(443)$). The ranges of $a_{CDOM}(443)$ and DOC concentrations for the regressions provided by M12 and Walker et al. (in press) and applied in this study were as follows: 0.018 m^{-1} < $a_{CDOM}(443)$ < 1.08 m^{-1}; 55 μ*M* < DOC < 500 μM, 0.39 < $a_{CDOM}(443)$ < 7.9 m^{-1}; 166 < DOC < 1660 μg L^{-1}).

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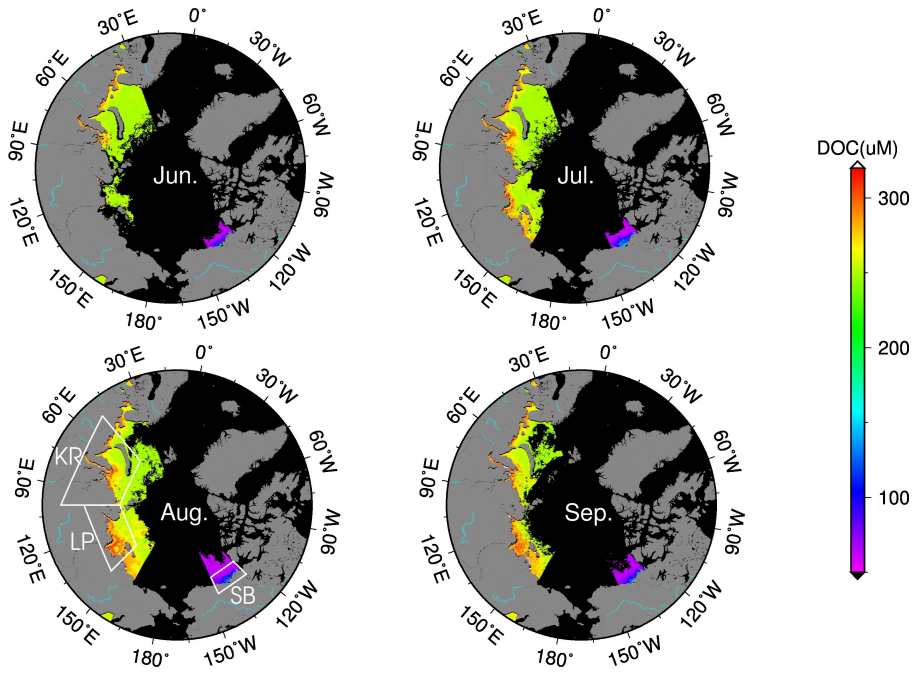

Fig. 11. Climatology of DOC concentrations in Arctic coastal waters (DOC^{sat}) from June to September, obtained by applying the DOC vs. $a_{CDOM}(443)$ regressions to the $a^{sat}_{CDOM}(443)$ images shown in Fig. 8. For WAO, the regression obtained by Matsuoka et al. (2012) was applied within the measured range of $a_{CDOM}(443)$ (i.e., $0.018 < a_{CDOM}(443) < 1.08\,m^{-1}$). For EAO, the regression obtained by Walker et al. (2013) was applied within the measured range of $a_{CDOM}(443)$ (i.e., $0.018 < a_{CDOM}(443) < 8.1\,m^{-1}$). To obtain those values, $a_{CDOM}(443)$ was estimated from $a_{CDOM}(350)$ by assuming $S_{CDOM} = 0.0175\,nm^{-1}$ for EAO (Aas et al., 2002; Stedmon et al., 2011). Histograms of DOC^{sat} values within the white boxes defined in Fig. 8 are shown in Fig. 12.

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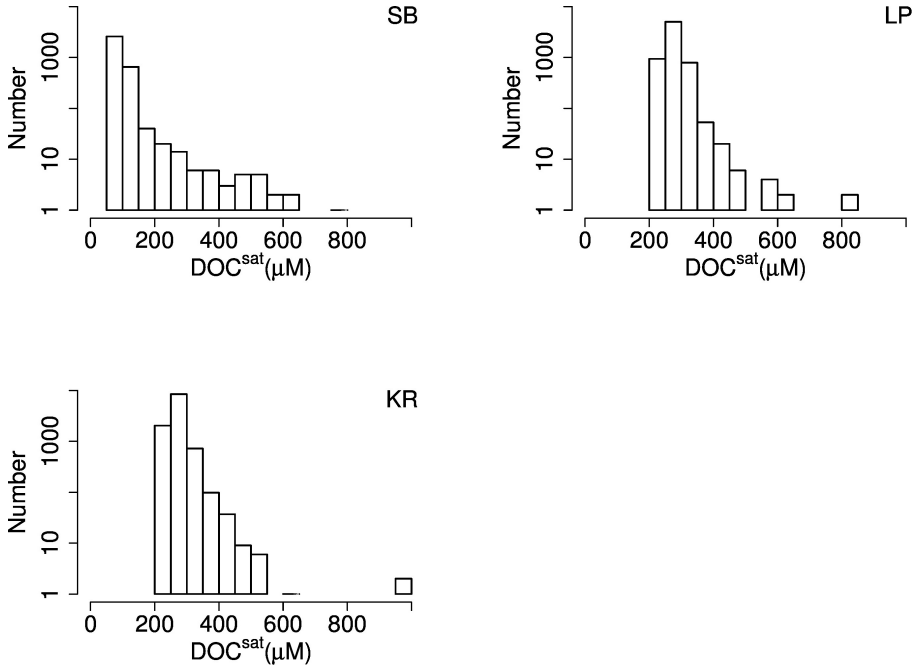

Fig. 12. Histogram of DOC^{sat} values in the SB, LP, and KR seas defined in Fig. 8.

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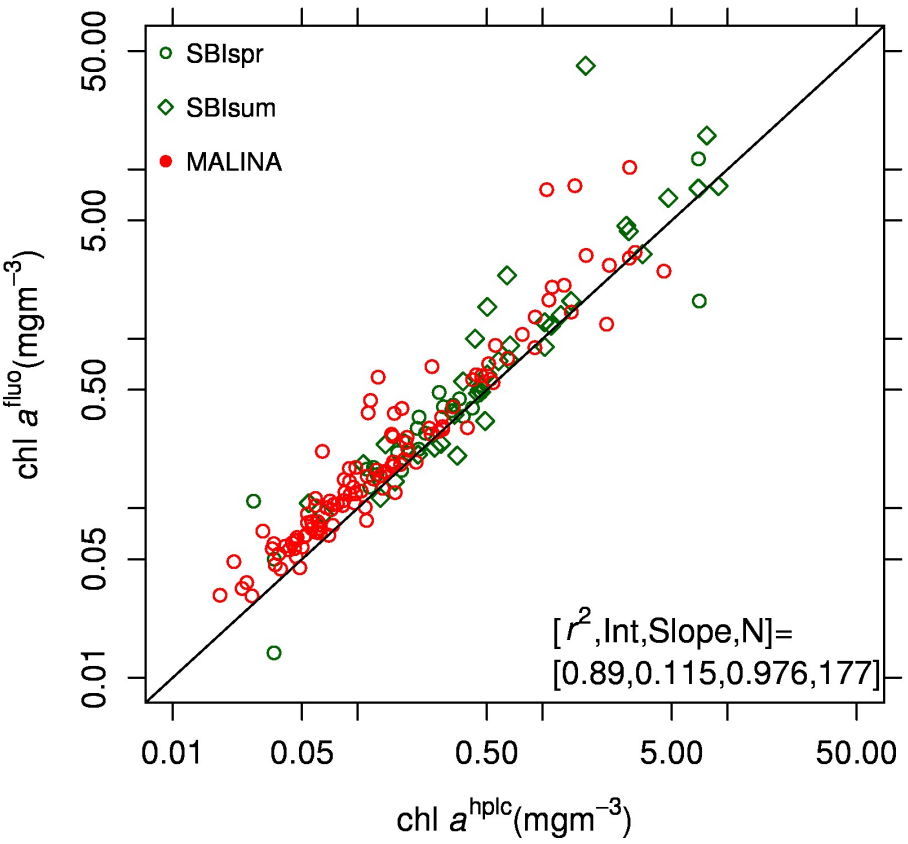

Fig. A1. Comparison of chl *a* determined fluorometrically (chl a^{fluo}) with chl *a* using HPLC method (chl a^{HPLC}).

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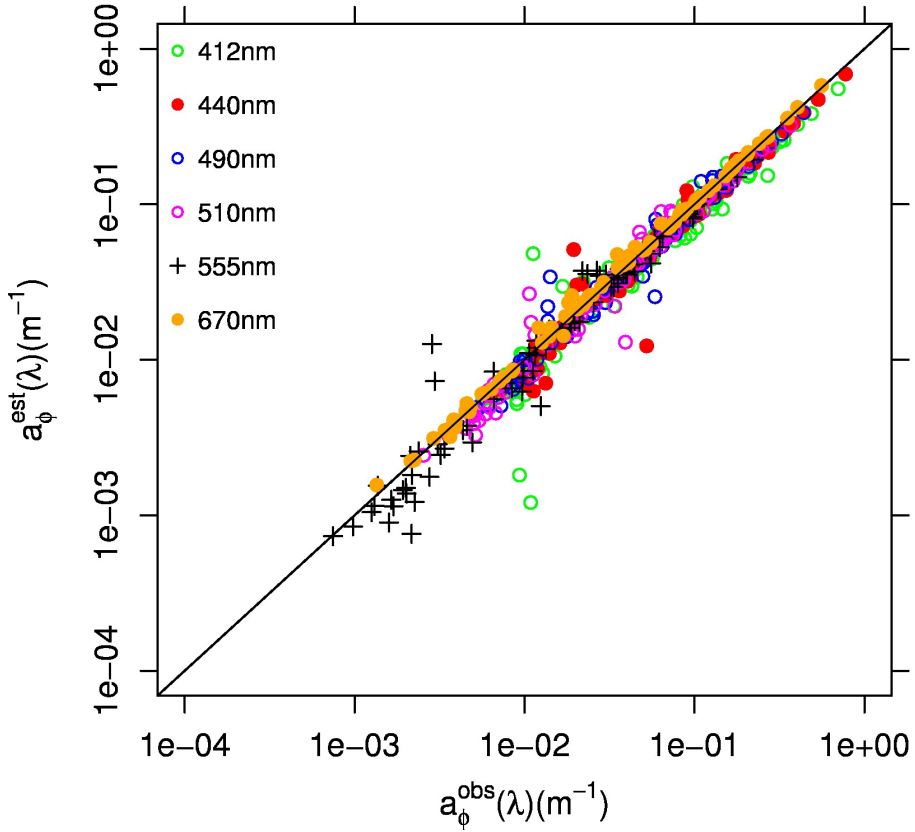

Fig. A2. Comparison of $a_\phi(\lambda)$ estimated using Bricaud and Stramski (1990)'s method with in situ measurements during the ICESCAPE1 cruise.

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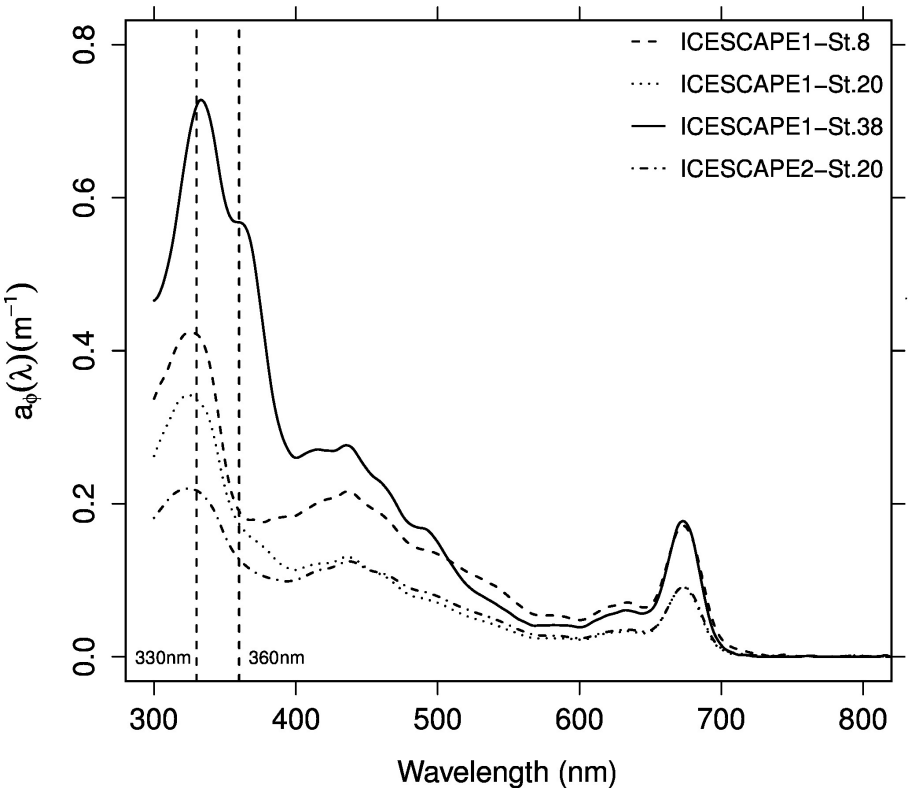

Fig. A3. Spectra of phytoplankton absorption coefficients ($a_\phi(\lambda)$, m^{-1}) at four stations during ICESCAPE1&2 cruises. CDOM absorption estimates at these points were outside of 50 % errors as shown in Fig. 7.

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