Input of organic carbon as determinant of nutrient fluxes, light climate and productivity in the Ob and Yenisey estuaries

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Spectral light attenuation profiles and concentrations of total and dissolved carbon (C), nutrients and chlorophyll a (Chl a) were studied along transects running from the river mouth to the Kara Sea during late summer 2003 for the Yenisey and fall 2005 for the Ob estuaries. Earth Observation data were used to generate composite images of water color and Chl a distribution over the estuaries and the Kara Sea to reveal the spatial impact of the river efflux in terms of optical properties.

High levels of total nitrogen (N), total phosphorus (P), silicate (Si) and iron (Fe), but low levels of inorganic N and P and Chl a were found in the estuaries. More than 90 % of total organic C was in dissolved form (DOC). The high concentrations of DOC, mostly terrigenous, humic compounds, gave extremely high attenuation coefficients for both visible and ultraviolet light. For UV-B, ZUVR (the depth at which 10% of surface light remains) was <10 cm, while ZUVR for visible light (PAR) generally ranged between 1 and 3 m for both transects. The light attenuation rapidly decreases when the freshwater is mixed with the coastal water outside off the coast. This leads to a strong light limitation and low productivity in the inner estuaries, while the high load of N and P associated with DOC eventually could promote primary production in the Kara Sea and further upstream the coastal current in the Arctic Ocean as the organic matter becomes diluted and photooxidized. On the other hand, the high inputs of colored dissolved organic matter (CDOM) provide an efficient screening of potential harmful UV-radiation over vast areas of the Arctic Ocean. A rising trend of riverine efflux to the Arctic seas is observed, and further increases in freshwater runoff as well as eventual permafrost thawing, will accentuate the freshwater impact in the estuaries and the Kara Sea.

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1. Introduction

The Arctic Rivers drain the tundra and taiga areas, and have among the world’s highest concentrations of dissolved organic matter (DOM) (Opsahl et al., 1999; Fütterer and Galimov, 2003). The areas drained by these rivers are estimated to hold a third of the world’s soil carbon in the permafrost tundra mires (Gorham, 1991; Dixon et al., 1994), and the Arctic shelf seas receive a freshwater input of approximately 4200 km3/yr (AMAP, 1998), corresponding to about 10% of the global river runoff (Aagaard and Carmack, 1989; Peterson et al., 2002) and hence also a significant flux of carbon in a global context. The Russian rivers Ob and Yenisey are two of the four largest rivers flowing into the Arctic. The Yenisey River is ranked 1st (603 km3/yr) and the Ob River is ranked 3rd (404 km3/yr) among the Arctic rivers in terms of freshwater discharge rates (AMAP, 1998). These rivers supply the shelf seas with nutrient-rich terrestrial and riverine matter. The Yenisei and Ob account for about 34% of the total Arctic river discharge and nearly 40% of the DOM output, corresponding to some 8–9 Tg C year−1 (Stein et al., 2003; Raymond et al., 2007). This allochthonous DOM is a carrier of organic carbon (C), but also of organic nitrogen (N) and phosphorus (P) as well as iron (Fe). The rivers are also the major source of silicate (Si) for marine recipients, yet Si is less linked with DOM compared to the other major nutrients. These rivers are also a major source of dissolved,
inorganic N and P from agricultural runoff and sewage. While the fluxes of N, P Fe and Si primarily support primary production in marine recipients, organic C fuels the heterotrophic bacterial activity. Hence, the balance between the inputs of organic C and other nutrients has a strong bearing on the net CO$_2$-balance of the ecosystem.

The output of colored terrigenous DOM impacts both the spectral properties and attenuation of light of the recipient marine waters, and the balance between nutrient availability and light attenuation in the estuaries governs the productivity of these systems. Further offshore, the major currents divert freshwater inputs eastwards and northwards along the Siberian coast and into the Arctic Ocean proper. Thus, the flux and dispersion of these elements are of vital importance for the ecosystem processes not only in the Kara Sea, but also in large upstream areas of the Arctic Ocean. The extent to which the effects of both nutrients and DOC will affect marine areas outside the estuaries depends on the nutrient uptake and production in the estuaries themselves as well as on the rates of bacterial utilization, photooxidation and DOM sedimentation. The spectral properties of the Arctic Ocean water suggest a pronounced influence of colored organic C over wide areas (Aas et al., 2001), reflecting that a major fraction of terrestrial DOC is recalcitrant to microbial breakdown and photo-oxidation (Amon and Meon, 2004). DOM is also to a large extent a carrier of organic-bound nutrients and the oxidation of DOM may also constitute an evolving source of primary production through a gradual release of bioavailable nutrients (Vähätalo and Zepp, 2005; Stedmon et al., 2007).

The flux of DOC from boreal catchments may range from 1 to 8 tonnes km$^{-2}$ yr$^{-1}$ (Hessen, 1999) depending on productivity and hydrology. Since the riverine DOM also is the main determinant of annual fluxes of N, P and to some extent also of Fe and Si, changes in hydrology per se as well as changes in the DOM-flux should have strong impacts on marine productivity. In addition, river discharge is crucial to the establishment of the Arctic Ocean’s halocline (Aagaard et al., 1981; Steele et al., 1995; Rudels et al., 1996; Schauer et al., 1997) and in the inter-hemispheric transport of freshwater (Wijffels et al., 1992) as well as bicarbonate for buffering against acidification (Riebesell et al., 2007). Nutrient fluxes from land to ocean integrate changes in terrestrial ecosystems, in land use, and in other human activities. The Ob and Yenisei rivers provide a huge supply of bio-reactive substances (nutrients, trace elements, DOC) that together with sunlight intensity regulates primary production in the adjacent coastal seas (Holmes et al., 2000). As yet, we have only an incomplete understanding of the fluxes of nutrients and other materials brought into the Arctic Ocean by rivers as well as by processes of coastal erosion (Reimnitz et al., 1994; Gordeev et al., 1996; Rachold et al., 2000).

During the past two decades, a major increase of freshwater runoff has been seen in the main Siberian Rivers (Peterson et al., 2002; Wu et al., 2005). This could further increase the overall impact of riverine outputs on the Kara Sea and further on the Arctic Ocean. The actual impact of the increased freshwater flux will however depend on whether it is yielding only a proportional dilution of nutrients or organic matter, or a real increase in these substances. Climate models predict significant warming in the Arctic in the 21st century, which will impact the functioning of terrestrial and aquatic ecosystems as well as alter land-ocean interactions in the Arctic (IPCC, 1998; Zwieback 2002). It has been predicted that the region will experience amplified effects of global climatic changes (Manabe and Stouffer, 1994). Estimated over the past decades (Peterson et al., 2002; Wu et al., 2005), a pronounced increase in freshwater discharge from the Arctic rivers can be, at least partially, linked to increased atmospheric concentrations of CO$_2$ causing a decrease of stomata density in plants and hence reduced evapotranspiration (Gedney et al., 2006). Global temperature increases will also cause decreases in snow cover albedo due to enhanced melting with increased heat absorption and permafrost thawing. This again would most likely cause not only intensified oxidation in the tundra peatlands and soils, but also a growing export of organic C as well as changes in the biological and chemical properties of the DOC (Kawahigashi et al., 2004).

To study the efflux of organic C and major nutrients from the estuaries of the major rivers Ob and Yenisei to off-coastal areas, we conducted two transect cruises from the river outlets to the open waters in both estuaries. By studying not only the concentrations of organic matter and nutrients but also solar attenuation and the spectral properties (radiometry) as well as the Chl$\alpha$ concentrations, we aimed to assess the role of river efflux in the productivity of the estuaries. The riverine impacts further off the coast were assessed by remote sensing. Previous MODIS imageries over the Kara Sea (Pozdnyakov et al., 2005a) have verified that this semi-enclosed Arctic Oceans shelf sea is strongly influenced by river discharge from the Ob and Yenisei rivers.

2. Materials and methods

2.1. Sampling programme and cruises

During the cruise from 14th to 29th of August 2003, 19 stations were sampled on the Ob-Yenisei shelf (Fig. 1). Emphasis was given to covering a transect from the Yenisei river mouth northwards across the salinity gradient from 0 to 35‰. During September 2005 a corresponding transect was made from the inner to the outer part of the Arctic Ocean (Peterson et al., 2002; Wu et al., 2005). This was further extended in 2005 by a longitudinal transect from the Yenisei river mouth north to the northern boundary of the shelf (Holmes et al., 2006). As yet, we have only an incomplete understanding of the fluxes of nutrients and other materials brought into the Arctic Ocean by rivers as well as by processes of coastal erosion (Reimnitz et al., 1994; Gordeev et al., 1996; Rachold et al., 2000).

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of the Ob estuary (Fig. 1). For both transects we obtained water samples for analysis of nutrients, Chl a, suspended matter and organic carbon as well as assessing the spectral properties of the water column. For reference purposes, CTD profiles and Secchi-depths were recorded at each station. These samples also served as “ground truth” data for the satellite based parameters. Various contaminants were also sampled along the same transect, but these results are reported elsewhere (Carroll et al., 2008)

2.2. Parameters and analysis

The hydrochemistry sampling programme consisted of collecting samples for total and dissolved nutrient concentrations and total organic carbon (TOC). Samples were collected from three different water layers (surface, middle depth and bottom). Exact sample depths were chosen based on water mass changes with depth as identified in the CTD profiles. Water samples were then collected directly from Niskin bottles mounted on the CTD unit. For Yenisey, both filtered and unfiltered samples were collected for the analysis of NH 4, NO 3, NO 2, PO 4, SiO 2 and Fe, while for Ob no fractionation was performed and hence only total N, P, Si and Fe was analyzed. To obtain the dissolved sample fractions from the Yenisey estuary, sub-samples were immediately filtered through individual 47 mm GFF filters. The volume of filtered water varied between 1000 and 2000 ml. Sample filters were then dried and stored at room temperature. Fe samples were preserved with HNO 3. SiO 2 samples were preserved with chloroform, PO 4, NH 4 and NO 2 + NO 3 samples were preserved with H 2 SO 4. The Fe, SiO 2, PO 4, NH 4 and NO 3 + NO 2 were stored at 5–10 °C. For measuring dissolved organic carbon (DOC), 3 ampoules (2 ml) of filtered surface water were collected and stored frozen for later analysis. As a back-up, 250 ml of surface water were filtered through a 0.2 µm Al 2 O 3 filter and stored for later analysis at 4 °C.

Total suspended matter (SM) samples were prepared by filtering 2000 ml of water through a pre-weighted 47 mm GFF filter. These filters were also stored at 4 °C. Samples for Chl a analysis were taken from the sea surface only. These 2000 ml sub-samples were filtered through 47 mm GFF filters and stored in liquid nitrogen. Yellow substance, which is a good proxy of the presence of humic material in seawater largely controlling the optical properties of the water column, were quantified from unfiltered water samples (100 ml) taken from the surface only. Samples for yellow substance were stored at 5–10 °C. In addition, water samples for the analysis of particulate C, N and P were filtered through 25 mm GFF filters. The volume filtered varied between 500 and 1500 ml depending on the particle load at each station. The filter was dried and stored at room temperature, and analyzed by standard procedures at the accredited laboratory of the Norwegian Institute for Water Research.

The spectral properties and sunlight attenuation in the water column was assessed by a four-channel radiometer (PUV Biospherical instruments, San Diego, US) at 4 UV wavelengths (308 nm, 320 nm, 340 nm, and 380 nm) and photosynthetic active radiation (PAR). Attenuation coefficients (Kd) were calculated for downwelling irradiance at different depths.

Downwelling irradiance at a certain depth z (Ed(z)) was given by Ed(z) = Ed(0) × e−Kdz. Care was taken to do the readings on the same side of the ship at all stations, and then avoiding shading effects. Kd's were estimated relative to surface light, and it was generally overcast during all samplings.

2.3. Satellite images

High quality satellite ocean color images (MODIS-Aqua data) for the Kara Sea were available from the NASA Ocean Color web site for August 2003 and also for the period prior to and right after the expedition. The MODIS-Aqua spectrometer sensor acquires images in the visible, and at high latitudes the revisiting frequency is one day. However, ice cover in early summer, dense cloudiness and ice edge haze as well as low sun zenithal angle in late summer constrains the number and quality of the remote sensing data available for analysis.

The images were processed with an advanced algorithm developed for a simultaneous retrieval of three water quality parameters: concentrations of phytoplankton Chl a, suspended minerals and dissolved organic carbon (Pozdnyakov et al., 2005b). The algorithm is based on the Levenberg-Marquardt multivariate optimization procedure and employs the relevant hydrooptical model. The model represents spectral cross sections of absorption and backscattering of pure water, phytoplankton, suspended matter (SM) and dissolved organic carbon (DOC).

To avoid inadequate retrieval results, the algorithm identifies and eventually discards the pixels with inaccurate atmospheric correction and/or pixels with the water properties incompatible with the applied hydro-optical model (Pozdnyakov et al., 2005b; Pozdnyakov et al., 2007).

The hydro-optical model initially established for Lake Ladoga (cf. Korosov et al., 2007) was used in this study. The model was assumed to be applicable on the following grounds: the waters of both water bodies are similar in terms of bogy areas, and the mineral and granulometric composition of sediments. It was not possible to develop a specific hydro-optical model for the Kara Sea due to lack of concurrent in situ optical and hydrochemical measurements. The specific feature of the applied algorithm do however allow for a separation between DOC, Chl a and SM due to the multivariate optimization. The accuracy of this differentiation and hence the accuracy of the respective concentration retrieval is determined by the adequacy of the applied hydro-optical model, however. The model is developed in such a way that the actual retrieved value is the concentration of DOM in mg C l−1. This was based on the assumption that the relationship between colored DOM in DOC is invariant for this water body. This assumption holds for Lake Ladoga, for which the model has been developed, and given the close correlation between CDOM and DOC also in the estuary (see below) it should hold here as well.

The retrieval accuracy of the algorithm was estimated in our several studies (Pozdnyakov et al., 2005b; Korosov et al., 2007, 2009). It was shown that the difference between satellite estimates of water quality parameters in coastal waters and ground-truth measurements is less than 50%. The percentage has been estimated as the module difference between measured and retrieved concentrations of the target water constituent (Chl a SM, DOC) normalized to the in situ concentration. Only qualified matchups were used for collecting this statistics. This has been done for many water bodies (see Korosov et al., 2009). The difference value is a statistical mean for each of the studied water bodies, which is then averaged over all water bodies. This indicates that the algorithm performs much better than the NASA standard algorithm for MODIS for case 2 waters, i.e. optically complex waters rich in Chl a, SM and DOC, as opposed to clear oceanic waters (case 1 waters), largely void of SM and DOC (Folkestad et al., 2007). The standard NASA SeaDAS algorithm OC4 retrieves the concentration of Chl a, and is not capable of yielding the other two products, viz. concentrations of SM and DOC; moreover, the concentrations of Chl a retrieved by OC4 for August 2003 proved to be unrealistically high (e.g. 30–60 µg l−1 in the Ob Bay and adjacent areas in the Kara Sea), while our algorithm restores the concentrations of Chl a, which are supported by the available historical data (e.g. Nöthig et al., 2003).
3. Results

3.1. Carbon and nutrients

Total organic carbon (TOC) was mainly made up by dissolved organic C (Yenisey: 95 ± 8 (StDev) %; Ob: 92 ± 9%), and, when excluding the freshwater (<0.1‰) samples, decreased monotonically with salinity in both the Ob and the Yenisey transects (Fig. 2). This TOC was almost entirely composed of terrestrially derived humic matter, reflected by the strong correlation between TOC and absorbance at 380 nm ($r^2$ = 0.99). Peak concentrations of TOC at both river outlets were close to 10 mg C l$^{-1}$. Both estuaries displayed high and similar concentrations of SiO$_2$ (close to 3 mg SiO$_2$ l$^{-1}$) and similar levels of dissolved Fe (mean 23 and 30 μg Fe l$^{-1}$) for Ob and Yenisey respectively, while the concentrations of total N, and especially total P were generally higher at the outlet of the Ob compared to the Yenisey. Average total P was 83 μg P l$^{-1}$ (range 34–163) for the Ob while 26 μg P l$^{-1}$ (range 10–48) for the Yenisey. Correspondingly, average total N was 306 μg N l$^{-1}$ (range 185–385) for the Ob and 270 (range 123–415) for the Yenisey. As for C, the major pool of N was in the dissolved fraction (Yenisey: 97 ± 11% for N and 67 ± 21% for P; Ob: 84 ± 1%).

For both estuaries, nutrient concentrations decreased with salinity, yet with far more scatter and less obvious linearity compared with TOC (Table 1), strongly indicating that various loss rates and transformations operated in addition to the dilution, and that these mechanisms also were different for the two estuaries. The relationship between total N and P and salinity was only marginally significant for both estuaries, and the concentrations of dissolved nutrients (Yenisey) were too low and scattered to provide strong trends over salinity. Both Si and Fe were negatively related to salinity, yet not in a linear fashion. The concentrations of Fe dropped rapidly from peak concentrations around 60 μg l$^{-1}$ at the inner stations of both estuaries, and levelled off around 20 μg l$^{-1}$ >5‰ (Fig. 3). SiO$_2$, on the contrary gave a bimodal response over salinity with peak concentrations close to 4 mg l$^{-1}$ around 10‰ for both estuaries.

![Fig. 2. Relation between total organic carbon (TOC) and salinity in the Ob (upper) and Yenisey estuary. Open symbols represent strictly freshwater samples (salinity below detection levels) and are omitted from the regression line.](image)

![Fig. 3. Fe (filtered samples) versus salinity. Smoothing spline fit (lambda = 100). Open symbols are freshwater samples.](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>$r^2$</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC Ob</td>
<td>$TOC = 7.8 - 0.21 Sal$</td>
<td>0.73</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>TotN Ob</td>
<td>$TotN = 345 - 4.46 Sal$</td>
<td>0.28</td>
<td>0.003</td>
</tr>
<tr>
<td>TotP Ob</td>
<td>$TotP = 99.0 - 1.78 Sal$</td>
<td>0.31</td>
<td>0.001</td>
</tr>
<tr>
<td>SiO$_2$ Ob</td>
<td>$SiO_2 = 3.9 - 42.4 Sal$</td>
<td>0.29</td>
<td>0.004</td>
</tr>
<tr>
<td>FilFe Ob</td>
<td>$FilFe = 36.5 - 0.25 Sal$</td>
<td>0.38</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Chla Ob</td>
<td>$Chla = 1.93 - 0.07 Sal$</td>
<td>0.4</td>
<td>0.05</td>
</tr>
<tr>
<td>Yenisey</td>
<td>$TOC = 7.8 - 0.17 Sal$</td>
<td>0.81</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>TotN Yenisey</td>
<td>$TotN = 308 - 2.08 Sal$</td>
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<td>0.03</td>
</tr>
<tr>
<td>TotP Yenisey</td>
<td>$TotP = 19.5 - 0.40 Sal$</td>
<td>0.22</td>
<td>0.004</td>
</tr>
<tr>
<td>SiO$_2$ Yenisey</td>
<td>$SiO_2 = 3161 - 19.8 Sal$</td>
<td>0.01</td>
<td>NS</td>
</tr>
<tr>
<td>FilFe Yenisey</td>
<td>$FilFe = 39.3 - 1.2 Sal$</td>
<td>0.32</td>
<td>0.002</td>
</tr>
<tr>
<td>Chla Yenisey</td>
<td>$Chla = 1.92 - 0.07 Sal$</td>
<td>0.4</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

![Table 1. Linear regression statistics for core parameters versus salinity.](image)
were no consistent patterns for elemental ratios along the transect. Concentrations of total suspended matter (TSM) in the Ob estuary ranged from 7 to 37 mg l\(^{-1}\) but showed no discernible pattern with salinity or TOC. Based on the concentrations in the inner estuary and the average annual discharge of water from Ob and Yenisey, we calculated approximate annual fluxes of all elements (Table 3).

Levels of Chla were low for both estuaries, 1.47 (\(\pm 0.68\)) l\(^{-1}\) for the Yenisey and 1.41 (\(\pm 0.10\)) l\(^{-1}\) for the Ob. Peak concentrations (close to 3 \(\mu\)g Chla l\(^{-1}\)) in both estuaries were recorded near the river mouth, suggesting that most of the phytoplankton biomass in fact was of freshwater origin.

### 3.2. Sea optics

Sea surface light penetration was extremely low at all stations along the transects. \(Z_{\text{obs}}\), the depth at which 10% of surface (air) radiation remained, ranged from near 10 cm at 320 nm, to 0.3–0.4 m at 380 nm (Fig. 5). Even for the spectrally integrated PAR, the average \(Z_{\text{obs}}\) was \(<2.5\) m for the Yenisey and only 1.5 m for the Ob. The diffuse attenuation coefficients were extremely high, ranging from about 25 m\(^{-1}\) at 320 nm to 1–1.7 m\(^{-1}\) for PAR with somewhat higher attenuation coefficients for the Ob estuary. The light profile remained fairly constant from the river mouth towards open water for the Yenisey transect (Fig. 6), and only at the outer station close to Novaja Semlja, did the water transparency increase substantially. For the Ob estuary, there was an apparent increase in transparency along the inner station, followed by a marked drop at the outer station, reflecting that the optical properties in this closed estuary are also determined by mixing processes. The strong

### Table 2: Correlation matrix for key parameters of Ob and Yenisey.

<table>
<thead>
<tr>
<th></th>
<th>Ob Salinity</th>
<th>Ob TOC</th>
<th>Ob Total N</th>
<th>Ob Total P</th>
<th>Ob SiO₂</th>
<th>Yenisey Salinity</th>
<th>Yenisey TOC</th>
<th>Yenisey Total N</th>
<th>Yenisey Total P</th>
<th>Yenisey SiO₂</th>
</tr>
</thead>
<tbody>
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<td>Salinity</td>
<td>1</td>
<td>-0.866</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-0.542</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TOC</td>
<td>-0.866</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total N</td>
<td>-0.622</td>
<td>0.377</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.305</td>
<td>0.379</td>
<td>0.771</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total P</td>
<td>-0.546</td>
<td>0.539</td>
<td>0.814</td>
<td>0.058</td>
<td>1</td>
<td>-0.105</td>
<td>0.426</td>
<td>0.823</td>
<td>0.748</td>
<td>1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-0.538</td>
<td>0.341</td>
<td>0.233</td>
<td>0.305</td>
<td>0.348</td>
<td>-0.566</td>
<td>0.559</td>
<td>0.305</td>
<td>0.348</td>
<td>-0.053</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.325</td>
<td>0.276</td>
<td>0.778</td>
<td>0.883</td>
<td>0.011</td>
<td>-0.105</td>
<td>0.426</td>
<td>0.823</td>
<td>0.748</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 3: Estimated annual fluxes in terragrams for TOC and major minerals based peak values (inner part of estuaries) and published data on discharge.

<table>
<thead>
<tr>
<th></th>
<th>Cons. mg l(^{-1})</th>
<th>Discharge km(^3)</th>
<th>Annual flux tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ob</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC</td>
<td>10</td>
<td>400</td>
<td>4</td>
</tr>
<tr>
<td>Total N</td>
<td>0.45</td>
<td>400</td>
<td>0.18</td>
</tr>
<tr>
<td>Total P</td>
<td>0.12</td>
<td>400</td>
<td>0.048</td>
</tr>
<tr>
<td>Total Si</td>
<td>3</td>
<td>400</td>
<td>1.2</td>
</tr>
<tr>
<td>Total Fe</td>
<td>2</td>
<td>400</td>
<td>0.8</td>
</tr>
<tr>
<td>Yenisey</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC</td>
<td>10</td>
<td>600</td>
<td>5.6</td>
</tr>
<tr>
<td>Total N</td>
<td>0.3</td>
<td>600</td>
<td>0.18</td>
</tr>
<tr>
<td>Total P</td>
<td>0.025</td>
<td>600</td>
<td>0.015</td>
</tr>
<tr>
<td>Total Si</td>
<td>3</td>
<td>600</td>
<td>1.8</td>
</tr>
<tr>
<td>Total Fe</td>
<td>2</td>
<td>600</td>
<td>1.2</td>
</tr>
<tr>
<td>NH₄+NO₂</td>
<td>0.012</td>
<td>600</td>
<td>0.0072</td>
</tr>
<tr>
<td>Dissolved P</td>
<td>0.019</td>
<td>600</td>
<td>0.0114</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>0.003</td>
<td>600</td>
<td>0.0019</td>
</tr>
</tbody>
</table>

Graphs and diagrams are shown for the analysis of the data.
attenuation also for PAR imply that the primary production is restricted to the very uppermost layers.

3.3. Remote sensing

The results of the retrievals of Chl\(a\), DOC and suspended matter from satellite data are illustrated in Figs. 7–9. Using Chl\(a\) as a proxy of primary production in the Kara Sea (summer 2003), we found that the predominant wind patterns yield a distinct eastern spread of river runoff from the Ob and Yenisei Rivers that boosts autotroph production. The concurrent spatial distributions of suspended matter (SM) and DOC comply very well with this observation as both constituents were most abundant to the east of the Ob estuary, and along the coastal zone between the Yenisei River and the Severnaya Zemlya Islands. Accordingly, the northern area of the south-western region of the Kara Sea is less influenced by freshwater inputs, and is also less productive. At the same time, as seen in the southeast part of the Kara Sea (Figs. 7 and 8), the warm Barents Sea waters appear as rich in Chl\(a\), and contain appreciable amounts of DOC, thus suggesting a positive impact of riverine inputs on the autotroph production in spite of the extremely low transparency.

While the range and distribution of DOC assessed from MODIS and ground measurements were in close agreement, the MODIS-based estimates of Chl\(a\) were almost an order of magnitude higher than the measured concentrations, reflecting the fact that the transect sampling was performed in late fall (hence low phytoplankton biomass) while the MODIS data represents composite images over the ice-free season including spring and summer blooming periods. Nevertheless the MODIS data clearly visualized the decreasing concentrations of Chl\(a\) along the transects.

4. Discussion

Our data confirm the findings of previous studies with regard to both concentrations and annual fluxes of TOC and DOC (Köhler et al., 2002; Dittmar and Kattner, 2003; Stein et al., 2003). Estimated fluxes based on such a brief time span of sampling should admittedly be judged with some caution, but estimated fluxes of total C (4 Tg yr\(^{-1}\) and 6 Tg yr\(^{-1}\) for the Ob and the Yenisey, respectively) are within the range of previous reports (Stein et al., 2002); also in Raymond et al., 2007 for flow-weighted discharge 2004–2005 (4.7Tg/yr\(^{-1}\) Yenisey, 3.1Tg/yr\(^{-1}\) Ob), yet somewhat higher than those given by Dittmar and Kattner (2003). Although, for the fluxes of total N our data exceeds those of Dittmar and Kattner (2003), and SiO\(_2\)-Si are in the upper range of previous estimates. Dissolved inorganic N (DIN: NO\(_3^–\) + NO\(_2^–\) + NH\(_4^+\)) and PO\(_4^{3–}\) however, are in the lower range of previous estimates.

For the Ob, there is a positive correlation between TOC and SiO\(_2\) as well as total N and total P, while for the Yenisey the picture is more scattered (Fig. 5): there was a significant positive correlation between TOC and SiO\(_2\) and TOC and total N, while a rather surprising negative correlation between TOC and Total P (or salinity and total P) in this estuary. Yet, all nutrients were assumed to be primarily of freshwater origin. Differential sedimentation rates, nutrient uptake and regeneration plus the turbulent dynamics in the estuary exhibited contrasting patterns for various nutrients and dissolved versus total pools of specific nutrients. Although SiO\(_2\) is clearly of freshwater origin, peak concentrations of SiO\(_2\) were found at medium salinity levels (Fig. 5) while for dissolved Fe there was an immediate drop, probably reflecting the turbulent dynamics in the estuary (Volkov et al., 2002).

By and large the Ob and Yenisey estuaries are rather similar with regard to carbon and nutrient concentrations, hence their relative export of elements to the Kara Sea can basically be scaled with annual discharge. The Ob has, however, twice as high concentrations of total P as Yenisey, probably reflecting somewhat different activities in the catchment, although this could also reflect that sampling in the Ob occurred in late fall when biological uptake had ceased. An overall higher concentration of PO\(_4\) in the Ob relative to the Yenisey (Dittmar and Kattner, 2003; Amon and Meon, 2004) do, however, indicate a higher relative P-export from this river.

While almost the entire fraction of TOC and SiO\(_2\) is in dissolved form, this is somewhat different for P and N. Close to 70% of total P (Ob estuary) was in dissolved form, however while the pool of dissolved P was on average 19 µg P\(^{-1}\), PO\(_4\) accounts for no more than 2.8 µg P\(^{-1}\), suggesting that some 85% of dissolved P was in the organic form. Almost the entire pool of N was in dissolved form (97%), while oxidized DIN (NO\(_3^–\) + NO\(_2^–\)) and reduced DIN (NH\(_4^+\)) together accounted for up to 23.7 µg/ P\(^{-1}\) or ~10% of dissolved N. For Fe, on the contrary, the major fraction was in dissolved form. The flux and fate of the various elements play a major role in productivity, light climate and the balance between autotrophic and heterotrophic processes in the estuary. While Fe rapidly precipitates at elevated salinity, SiO\(_2\) and the dissolved organic fractions of

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**Fig. 5.** Light responses of different wavelengths represented as depths where 10 % of surface light remains (Z\(_{10\%}\) depth) and vertical attenuation coefficient (K\(_{d}\) lower).

**Fig. 6.** Z\(_{10\%}\) for PAR along the transects from the river mouth to the oceanic stations.
C, N and P can be transported over vast areas, gradually becoming available to autotrophs after photo-oxidation and microbial degradation.

The relationship between CDOM and salinity in estuaries will depend both on flushing rate and internal processes (cf. Bowers and Brett, 2008), yet in the large estuaries of Ob and Yenisey DOC or humic substances decrease monotonously with increased salinity with only limited losses by flocculation (cf. Amon and Meon, 2004), reflecting a straightforward dilution of this assumed recalcitrant organic C. Within the estuaries, the DOC-concentrations are rather conservative, and long-term incubation experiments indicate low bacterial mineralization rates (Köhler et al., 2002; Amon and Meon, 2004).
While photooxidation at times may represent significant losses of DOC. Under clear sky, Amon and Meon (2004) reported losses of 40 µM DOC or 6% of total DOC over a course of 290 h. It should be kept in mind, however, that owing to the extremely high attenuation of short-wave light, such mineralization rates are only valid for the upper few centimetres. Also, for most of the year, conditions for photooxidation are poor or absent.

Even though a certain fraction of DOC certainly is lost by combined microbial breakdown and photooxidation, most of the Kara Sea and the entire Arctic ocean are characterized by high attenuation of short-wave radiation. In the inner part of the estuaries, the high attenuation coefficients for PAR as well will pose constraints on primary production. In the offshore areas, however, the elevated levels of DOC will provide an efficient sunscreen for harmful UV radiation. Z\text{10\%} level at 380 nm are typically around 10–20 m for most of the Norwegian Sea, Greenland Sea and Barents Sea, and rarely <5 m even for coastal areas (Aas et al., 2001). In contrast, Z\text{10\%} 380 nm for the estuaries was on average 0.3 m, exceeding 0.5 m only at the outer stations. This fits well with previous estimates of mean Z\text{10\%} 380 nm for the Ob and Yenisey estuaries (0.2 m) reported by Aas et al. (2001). These authors also reported 2.2 m as the average value of Z\text{10\%} 380 nm for the Kara Sea as a whole.

The Chla concentrations found in our study (0.4–3.4 for the Ob, 0.6–2.9 for the Yenisei) fits well those of Nöthig et al. (2003), and the marked drop in Chla along the transect suggest that most of the autotrophs in the estuary are of freshwater origin (cf. Makarevich et al., 2003). Both the salinity stress and low sunlight levels could thus constrain primary production in the estuary, and also pose constraints on bacterial mineralization of DOC (Langenheder et al., 2003). Further off coast, a gradual oxidation of humus-bound, organic N and P could stimulate both autotroph and heterotroph production, as indicated by the remote sensing data, and also shield vast areas from harmful UV-R.

Division of the marine and the riverine water masses are clearly seen in the satellite images. The frontal zones are located across the gradients of TOC and suspended matter, which can be used as a passive tracer for extent of the riverine waters (Figs. 8 and 9). It is seen in Fig. 7 that this frontal zone limits the extent of the areas with high Chla concentrations. Importantly, the maximum blooming occurs not in the entire Ob Bay, but only in the mixing zone where turbid brackish waters are diluted with cleaner saline waters. Further south, where waters are almost opaque due to the extremely high DOC and SM content, Chla concentrations are lower.

DOC and suspended matter exhibits similar behaviour in the outer part of the Ob bay and in the open front of the estuaries — its concentrations are high only within the area of riverine waters invasion (Fig. 8 and 9). Clearly, the TOC content in the Ob Bay only increases towards the south. The adequacy of the retrievals for TOC was confirmed by our ground truth data, which also compare well with previous shipborne determinations (Köhler et al., 2002; Gaye-Haake et al., 2003; Nöthig et al., 2003). For Chla, however, the remote sensing estimate should be read with some caution, although the major reason for the inconsistency between measured chla and MODIS-derived chla is likely that the transect sampling was performed in late fall (hence low phytoplankton biomass) while the MODIS data represents binned, composite images over the ice-free season including spring and summer blooming periods.

The huge drainage basins of these rivers are under change. Increased levels of CO2 and permafrost thawing may in concert increase both the discharge and also levels of TOC, and thus associated nutrients. Permafrost thawing will most likely increase substantially the concentrations of TOC (e.g. Freeman et al., 2004; Frey and Smith, 2005), as well as accompanied by increased runoff (Peterson et al., 2002; Wu et al., 2005). The net effect of these changes on productivity and C-sequestration in the Arctic ocean is not straightforward, since TOC per se will likely stimulate the heterotrophic activity: increased nutrient loads lead to a stimulation of the primary production, but can also enhance TOC mineralization rates. These conditions will likely cause an increase in heat absorption in the top-most layer of the water column, increasing thermal stability and producing a shallower location of the
thermoline. Together these conditions are expected to strengthen the “sun-glass” protection of marine biota from shortwave radiation. Finally it should be kept in mind that in the long term, new production in marine areas ultimately depends on freshwater inputs of P, Si and Fe which again regulates the marine C-sequences (cf. Lenten and Watson, 2000). These nutrient supplies connected to freshwater inputs also enhance alkalinity and hence buffer against CO2-induced marine acidification.

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Appendix A. Supplementary data

The supplementary materials associated with this article can be found in the online version, at doi:10.1117/12.791126.

References


