Dissolved organic matter (DOM) in the estuaries of Ob and Yenisei and the adjacent Kara Sea, Russia

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Abstract

Based on observations during four scientific expeditions to the Kara Sea and the Siberian rivers Ob and Yenisei we determined the discharge, distribution and characteristics of dissolved organic matter (DOM). Surface concentrations of dissolved organic carbon (DOC) ranged from 151 µM C in the northern Kara Sea to 939 µM C in the river Ob. The estimated annual mean DOC concentration in the Yenisei (681 µM C) was slightly higher than in the Ob (640 µM C). Dissolved organic nitrogen (DON) concentrations typically varied between 5 and 15 µM N with higher values in the rivers. Freshwater discharge and DOC concentrations experienced pronounced seasonal variations strongly affecting the spatial and temporal distribution of DOM in the Kara Sea. The largely conservative distribution of DOC and DON along the salinity gradient indicated the predominantly refractory character of riverine DOM. This observation was consistent with laboratory experiments, which showed only minor losses due to flocculation processes and bacterial consumption. Optical properties and relatively high C/N ratios (19 to 51) of DOM suggest that a large fraction of river DOM is of terrestrial origin and that phytoplankton contributed little to DOM on the Kara Sea shelf during the sampling periods. Together, the rivers Ob and Yenisei discharge about 8 Tg DOC yr^{-1} into the Kara Sea. Due to the absence of efficient removal mechanisms in these estuaries the majority of riverine DOM appears to pass the estuarine mixing zone and is transported towards the Arctic Ocean.

1 Introduction

Dissolved organic matter (DOM) is one of the largest active pools of organic carbon on earth and hence plays an important role in the global carbon cycle. Some recent estimates suggest that the amount of dissolved organic carbon (DOC) in the oceans is 700 x 10^{15}g C, compared to 570 x 10^{15}g of carbon within terrestrial biota (Hedges et al., 1997). Because of its immense size, even small changes in the DOM pool can lead to significant perturbations of the global carbon cycle. Rivers annually transport 0.4 x 10^{15} g organic carbon from the

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continents to the oceans (Hedges et al., 1997). The Arctic Ocean receives about 11% of the freshwater and DOM supplied globally by rivers (Gordeev et al., 1996; Shiklomanov et al., 2000; Rachold et al. 2003) although it represents only 1% of the global ocean volume (Shiklomanov, 1998). Thus, the freshwater discharge into the Arctic Ocean by rivers is the highest on a volume basis among the world oceans.

More than 40% of the freshwater supply and about 35% (7-9 x 10^{12}g C yr^{-1}) of the total organic carbon (TOC) discharged to the Arctic Ocean are contributed by the rivers Ob and Yenisei (Telang et al., 1991; Gordeev et al., 1996; Gordeev and Tsirkunov, 1998; Opsahl et al., 1999). Both rivers drain large areas (5.5 x 10^6 km^2) of the northern hemisphere, particularly vast regions of the Russian tundra and taiga (Pavlov and Pfirman, 1995). Recent estimates suggest that up to 30% of the global soil organic matter resides in the Kara Sea drainage basin (Dixon et al., 1994; Bleuten et al., 2000). Hence, Ob and Yenisei could represent an important link between the terrestrial and marine organic carbon pools in light of global change. Most of the large Arctic rivers, the Mackenzie being a notable exception, have characteristically high DOC concentrations and relatively low sediment loads, thus DOC is by far the dominant (> 90%) form of organic carbon transported to the Arctic Ocean by rivers (Opsahl et al., 1999; Lobbes et al., 2000; Rachold et al. 2003).

Before entering the Arctic Ocean, riverine DOM is subjected to biological, physical, and chemical transformation processes such as bacterial decomposition, flocculation and photolysis (Sholkovitz, 1976; Thurman, 1985; Spitzy and Leenheer, 1991; Mopper and Kieber 2000). These mechanisms are particularly pronounced in estuaries of shallow shelf seas, where waters with different chemical, physical and biological characteristics mix. Because of its immense freshwater input and its extended shelf area the Kara Sea is an ideal location to study these transformation processes (Amon and Spitzy, 1999). Due to the selective removal of suspended and dissolved compounds from river water, the estuarine mixing zone has also been termed "marginal filter" (Lisitzin, 1995). In Arctic shelf regions these processes are mainly restricted to the summer season because the river discharge and the organic matter supply to the marginal filter zone as well as the biological activity are strongly reduced during winter (Lisitzin, 1995). The fate of terrestrial DOM in estuaries remains poorly understood. Various field studies (Moore et al., 1979; Mantoura and Woodward, 1983; Cadee et al., 1993; Cauwet and Sidorov, 1996; Kattner et al., 1999) have indicated the conservative behavior of DOM, suggesting a significant contribution of riverine DOM to the oceanic DOM pool. Other investigations (Sholkovitz, 1976; Ertel et al., 1986; Artemyev and Romankevich, 1988) have shown the removal of riverine DOM fractions in estuaries by flocculation or sorption, thus reducing the contribution of riverine DOM to the oceanic DOM pool.

One of the big unsolved questions in contemporary biogeochemistry is the fate of terrestrial-derived DOM in the world oceans (Hedges et al., 1992; Hedges, 1997; Opsahl & Benner, 1997). Based on riverine inputs alone, the entire oceanic DOM pool would be replaced by terrestrial DOM in less than 3000 years, but paradoxically only trace amounts of terrestrial DOM can be detected in the oceans interior (Opsahl & Benner, 1997). Either our estimates are grossly in error or there exists a so far unrecognized removal mechanism for riverine DOM in the ocean (Hedges et al., 1997). The present study specifically addresses the fate of riverine DOM during estuarine mixing in the Ob and Yenisei estuaries. In order to improve our understanding of DOM dynamics within the estuaries we determined bulk chemical and optical parameters to identify sources and pathways of DOM in the Kara Sea.

Based on recent information on seasonal freshwater discharge and available information of seasonally varying DOC concentrations we will present annual DOC flux estimates for Ob and Yenisei.

2 Material and Methods

2.1 Study site and hydrology

Of all the Arctic shelf seas the Kara Sea is most influenced by continental run off, receiving more than one third of the total freshwater discharged to the Arctic Ocean (Pavlov and Pfirman, 1995 and references therein). The total amount of annual freshwater input to the Kara Sea equals roughly 1340 km^3, predominantly contributed by the rivers Ob (400 km^3 a^{-1}) and Yenisei (630 km^3 a^{-1}; Pavlov and Pfirman, 1995; Gordeev and Tsirkunov, 1998). Considering the 200 m isobath as the northern border, the Kara Sea encompasses an area of about 883.000 km^2 with a water volume of 98.000 km^3 (Pavlov and Pfirman, 1995). Accordingly, the freshwater input would theoretically fill the entire Kara Sea basin within 73 years. However, due to the strong vertical density gradient, the freshwater lens remains in the upper 20 m, resulting in much shorter residence times (3.5 ± 2 years; Schlosser et al., 1994) for river water on the shelf. Due to the continental climate in the drainage basins of Ob and Yenisei, both rivers are characterized by a typical Siberian water regime. Soon after thawing the rivers discharge increases to maximum values in May or June (Fig. 1).

The hydrographs are therefore characterized by a pronounced discharge peak in spring and a relatively low water flow between September and April (Fig. 1). The hydrograph of the Yenisei has a more pronounced seasonal maximum discharging more than 30% of its annual discharge in June. The Ob shows a more balanced hydrograph with highest discharge in June, July and August (Fig. 1). The annual discharge of the Yenisei consists of 50% snowmelt, 35% rain and only about 15% are contributed by base flow from groundwater (Gitelson et al., 1988; Telang et al., 1991; Pavlov and Pfirman, 1995). The water supply of the Ob is also dominated by snow and rain in summer, whereas the winter baseflow derives predominantly from groundwater (Pavlov et. al., 1994; Lisitzin, 1995). In general, seasonal variability observed in river runoff was clearly larger than interannual variability between "wet" and "dry" years (Fig. 1). Ob (2.99 x 10^6 km^2) and Yenisei (2.58 x 10^6 km^2) drain vast regions of the Russian tundra and taiga. However, a large proportion of the water entering the Kara Sea originates far beyond the limits of the Arctic territory, as far south as 40° N (Shiklomanov et al., 2000). A significant part of the Kara Sea drainage basin is located in the region of the plain tundra relief with a dominance of broad swampy lowlands (Lisitzin, 1995; Gordeev et al., 1996). These boggy soils of the West Siberian Lowland represent an enormous potential carbon source. About 50% of the worlds peat resources are located in the West Siberian Lowland. The total amount of carbon stored in West Siberian peat is estimated to be 51 x 10^{15} g C (Bleuten et al., 2000). Large parts of the Ob's drainage basin, including the worlds largest bog system, the "Great Vasyugan Mire" (5.4 million hectares), are dominated by these peatlands. The Yenisei basin also drains parts of the Siberian Lowlands, but the predominant part of the catchment area is covered by multiyear frozen rock (Gitelson et al., 1988; Pavlov et al., 1994).
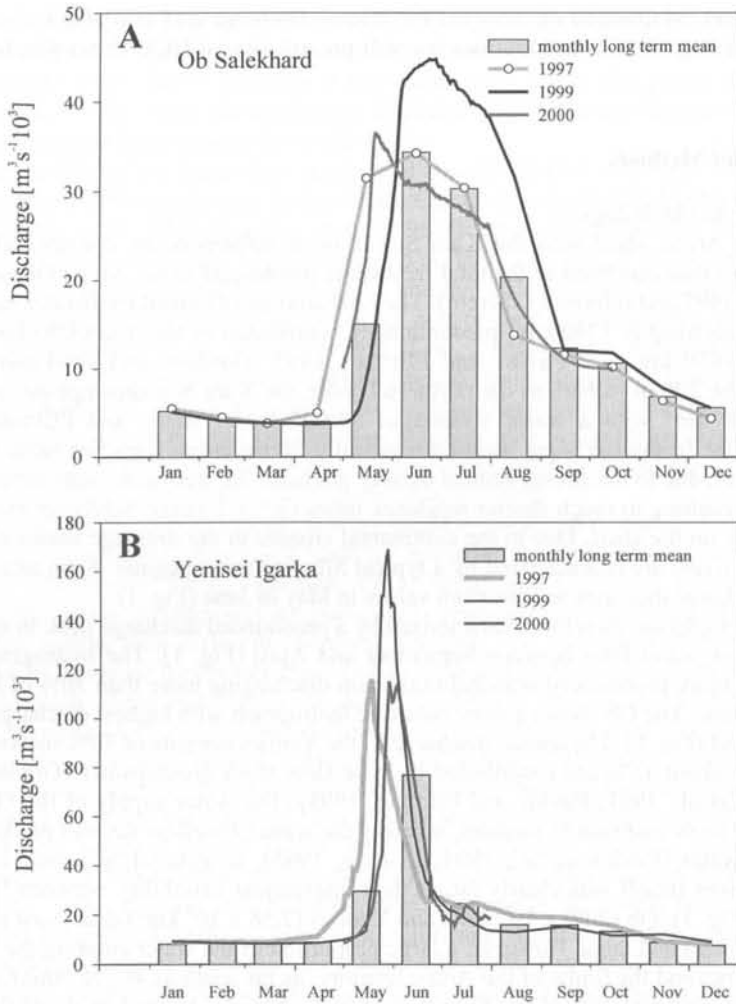
Fig. 1: Hydrographs at the downstreammost gauge stations Salekhard (Ob) and Igarka (Yenisei). Lines represent the discharge of the years during which samples were taken, columns represent the long term monthly mean discharge (1980-1999).

2.2 Sampling

Fieldwork was carried out in the framework of the joint Russian-German project 'Siberian River Run-off' (SIRRO) during 3 cruises of the R/V "Akademik Boris Petrov" between August and September in 1997, 1999 and 2000. Additional samples were collected in June 2000 near Salekhard during a land-based expedition to the Ob. Sampling focused on the salinity gradient in the estuaries of Ob and Yenisei in 1997 and 1999. During the BP 2000 expedition the sampling program was extended to the outer Kara Sea as far North as 77°N (Fig. 2).
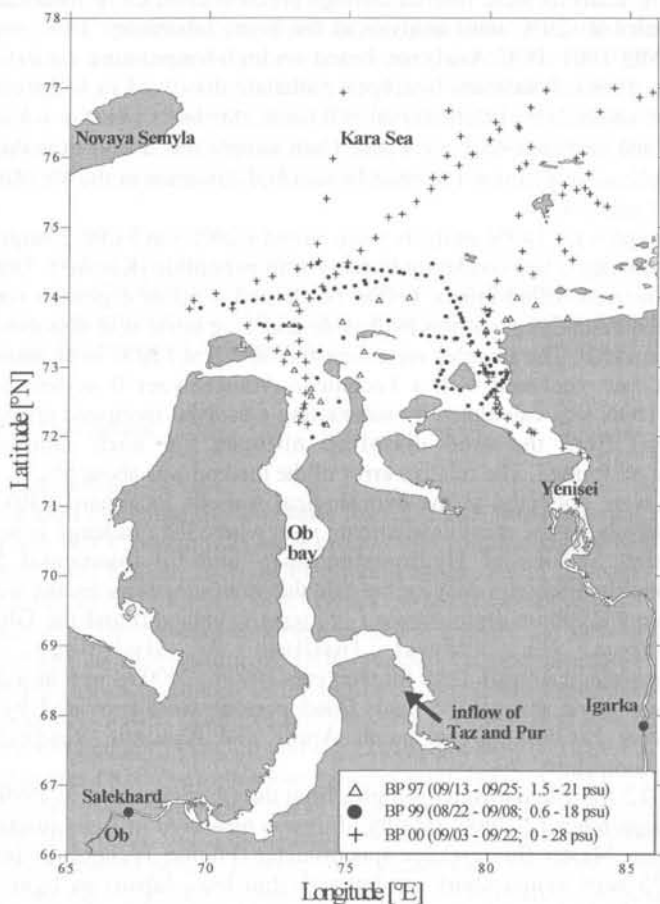

Fig. 2: Location of sampling sites during the cruises of RV "Akademik Boris Petrov" in 1997 (BP97), 1999 (BP99) and 2000 (BP00).

Surface samples covered a salinity range from freshwater (0.0) to more than 28 in the northern central Kara Sea. Samples were taken using a CTD-rosette-sampler at all major hydrographic stations. To increase spatial resolution, additional surface samples were collected using clean buckets. During the land expedition to the Ob River near Salekhard surface and bottom samples were collected at three locations across the river using a Ruttner standard water sampler. For further details on sampling see Matthiessen and Stepanets (1998), Stein and Stepanets (2000), Stein and Stepanets (2001) and Holmes et al. (2001).

2.3 Measurements

Samples for DOC analysis were filtered through precombusted GF/F filters and stored in sealed glass ampoules at -20°C until analysis at the home laboratory. DOC samples were analyzed using a MQ 1001 TOC Analyzer, based on high-temperature catalytic oxidation (Qian and Mopper, 1996). Potassium hydrogen phthalate dissolved in UV treated Milli-Q water was used for calibration. International reference standards (44.0 ± 1.5 µM C) were routinely analyzed and averaged 45.4 ± 1.4 µM. Each sample was analyzed in duplicate with a minimum of 3 replicate injections. The relative standard deviation at the 400-800 µM DOC level was between 1 and 2%.

GF/F filtered samples for DON analysis were stored (-20°C) in FLPE (Nalgene) bottles. DON was measured using a wet oxidation method with persulfate (Koroleff, 1983). Twenty milliliters of sample were filled into a Teflon bottle and 3 ml of digestion reagent (25 g potassium peroxodisulfate, 7.5 g sodium hydroxide and 15 g boric acid dissolved in 500 ml Milli-Q water) were added. The samples were digested for 2 h at 120°C in an autoclave. Total dissolved nitrogen was measured with a Technicon Autoanalyzer II system according to standard methods. DON was calculated by subtracting dissolved inorganic nitrogen (nitrate, nitrite, ammonium) from the total dissolved nitrogen. For each sample duplicate measurements were performed. The relative error of the method was about 5%.

Discharge data were collected at the hydrological stations Salekhard (Ob) and Igarka (Yenisei; Fig. 2), which are the most downstream sites where the discharge is monitored by the Federal Russian Service of Hydrometeorology and Environmental Monitoring (Roshydromet). Monthly discharge data for the calculation of long-term means were obtained from the R-Arctic-net database (http://www.r-arcticnet.sr.unh.edu) and the Global Runoff Data Centre from the Federal Institute of Hydrology, Germany (http://www.bafg.de/welcome.html). Data for the years 1997 to 2000 as well as a data set with higher temporal resolution during the peak flood periods were provided by the Water Resources and River Estuaries Department, Arctic and Antarctic Research Institute/ University of New Hampshire.

Fluorescence of 0.2 µm filtered water samples from the Ob (September 2, 1999; salinity of 0.6) and Yenisei (September 12, 2000; salinity of 0) was measured in 1 cm quartz cuvettes at 18 °C using a Quanta Master fluorescence spectrometer (Photon Technology International) equipped with a 75 watt xenon short arc lamp (Ushio Inc., Japan) as light source and monochromators for both the excitation and emission sides. The samples were diluted 2-3 fold with Milli-Q water prior to analysis in order to minimize quenching of fluorescence by inner filter effects. Excitation/emission matrices (EEMs) were generated by concatenating 42 individual emission spectra collected in ratio mode at excitation wavelengths between 260 and 465 nm using 5 nm increment steps. The first emission scan covered the spectral range from 272 to 492 nm and the last from 477 to 697 nm with data collected every 1 nm over an

interval of 0.5 s. Photomultiplier voltage was set to 1000 V and bandpass widths were 5 nm for excitation and 2 nm for emission, respectively. Individual spectra were corrected for the water Raman scatter peak. Correction for excitation (based on Rhodamine B as quantum counter) and emission characteristics of the instrument were performed electronically by the software of the instrument. The fluorescence intensity (Ex/Em =350/450) of a standard solution of 1 ppb quinine sulfate in 0.05 M sulfuric acid (measured under sample conditions and corrected for solvent fluorescence) was used to convert sample fluorescence to quinine sulfate units (QSU).

2.4 Flocculation experiment

To estimate the importance of flocculation processes on DOM concentration during estuarine mixing we performed a mixing experiment during the BP 2000 cruise. Water from the Yenisei (salinity of 0.0) was mixed with Kara Sea water (salinity of 33.8) in various proportions in polypropylene-containers (20L) to salinities of 0, 3, 6, 9, 15, 25 and 33.8. After 27 h the experiment was terminated and subsamples were filtered through precombusted GF/F-filters to obtain samples for DOC and POC analysis.

2.5 Bacterial decomposition experiment

In order to study bacterial utilization of riverine DOM, 30 l of Yenisei water (0) was filtered (0,6 µm) and stored in the dark at ambient temperature (4 °C) in a PP-bottle. We monitored the concentration of DOC over a period of 21 month with higher sampling frequency at the beginning of the experiment.

3 Results and Discussion

3.1 Surface distribution of DOC

Due to the high discharge of freshwater from Ob and Yenisei during the spring flood the entire Kara Sea was characterized by a pronounced riverine signal with low surface water salinities (Amon and Köhler, 2000; Köhler and Simstich, 2001) during all summer - early fall sampling periods. In 1997 surface DOC values ranged between 316 µM C (at salinity of 21) in the northwestern part of the sampling area and 558 µM C (at salinity of 2) in the Yenisei Estuary. The spatial distribution of DOC surface concentrations in 1997 reflected the prevailing north-eastward currents in the estuaries during late September (Fig. 3A; Harms et al., 2000). Slightly higher values (458-558 µM C) were observed in the Yenisei Estuary relative to the Ob Estuary (317-520 µM C). During the BP-99 cruise in August - September we observed higher DOC concentrations ranging from 498-721 µM C in the Yenisei Estuary and from 358-567 µM C in the Ob Estuary at approximately the same salinity ranges (salinity of 1-18) as in 1997 (Fig. 3B). The riverine currents were directed towards the central Kara Sea during this sampling period. Lowest DOC values were observed during the BP-00 cruise in the outer Kara Sea (Fig. 3C), where the influence of both rivers weakened as indicated by surface salinities > 28. However, even in the northernmost part of the study area DOC concentrations ranged between 151 and 200 µM C (Fig. 3C), which is still about twice the concentration generally observed in Arctic Ocean surface waters (e.g. Wheeler et al., 1997; Guay et al., 1999; Opsahl et al., 1999; Amon and Benner, submitted). Maximum DOC values in the Yenisei (713 µM) were found near 71°00' N at zero salinity on September 12th during the BP-00 cruise (Fig. 3C). The respective ranges for DOC concentrations in the estuaries of

Yenisei and Ob in September 2000 were 151-713 µM C (salinity of 0-28) and 186-503 µM C (salinity of 9-26). In general, the observed surface DOC values were in good agreement with published data from Arctic rivers and adjacent shelf seas (Cauwet and Sidorov, 1996; Lara et al., 1998; Opsahl et al., 1999; Kattner et al., 1999; Lobbes et al., 2000).

The temporal variability of DOC concentrations on the surface was high, even within the relatively short sampling periods (~3 weeks). Reasons for the observed temporal variations of DOC include changes in current directions on the shelf, which switch from a north-westward to an eastward direction during summer (Harms and Karcher, 1999; Harms et al., 2000), and the high seasonal discharge fluctuations, particularly during the peak flow period (May – July). DOC variability became evident when samples were repeatedly collected at similar positions at different times during the sampling period (2 – 3 weeks apart; Fig. 3B, C). During BP-00 we observed a decrease of DOC surface concentrations by about 35% within a period of only 3 weeks in the Ob Estuary (Fig. 3C). Similar temporal differences in DOC were observed throughout the BP-99 cruise near 74° 30`N and 76° 00`E (Fig. 3B). Surface salinity data of the BP-99 and BP-00 cruises (Amon and Köhler, 2000; Köhler and Simstich, 2001) confirmed the strong seasonal and interannual variability of surface water masses in the Kara Sea during summer.
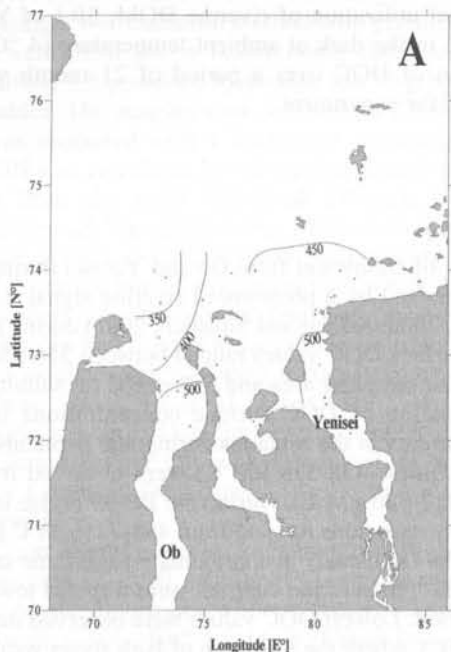

Fig. 3a: Surface distribution of DOC [µM C] during the cruise in 1997. The highly dynamic nature of DOC concentrations in the system is indicated by different DOC values at almost identical positions but different sampling dates (3 weeks apart). The discrete numbers in B and C represent samples taken at the very beginning of the sampling periods, the isolines are based on the residual samples.
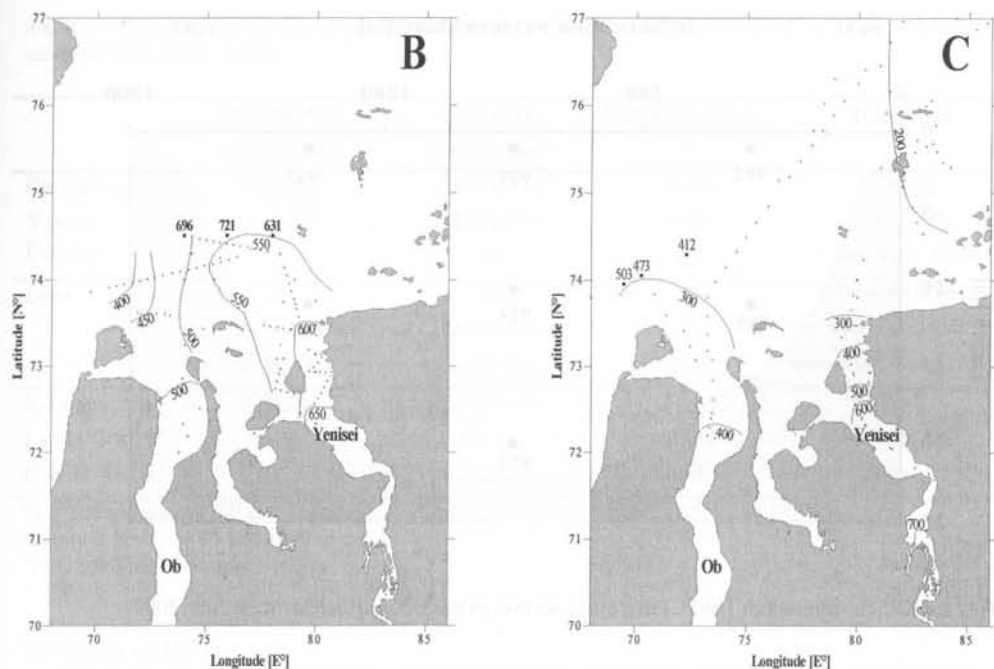
Fig. 3b and c: Surface distribution of DOC [μM C] during the cruises in 1999 (B) and 2000 (C). The highly dynamic nature of DOC concentrations in the system is indicated by different DOC values at almost identical positions but different sampling dates (3 weeks apart). The discrete numbers in B and C represent samples taken at the very beginning of the sampling periods, the isolines are based on the residual samples.

During the land-based expedition to the Ob near Salekhard in June 2000 we had the opportunity to collect samples in the Ob close to peak discharge season. Very high DOC concentrations of up to 939 μM C were observed at this sampling occasion about 3 weeks after the discharge maximum (Fig. 4). The differences of DOC concentrations within the cross-section profile were relatively small, with values ranging between 869 and 939 μM C. Due to the sampling date directly after the peak flood, the river water was apparently well mixed throughout the water column. Surface concentrations in the main channel were slightly higher than values in the western part of the transect and in deeper samples. The concentrations observed in the river Ob in June were much higher than the DOC values observed in the Ob bay later in the season at low salinity also pointing to a high temporal variability of DOC within this system.
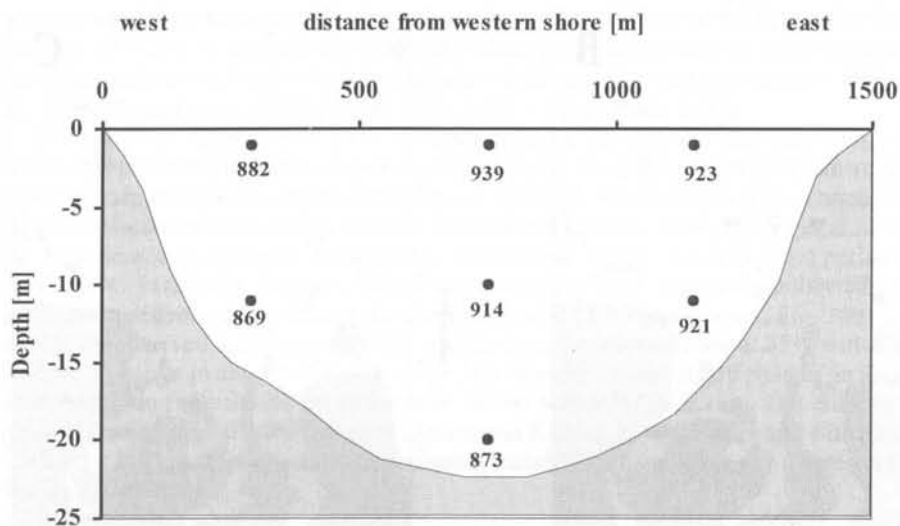
west   distance from western shore [m]   east

Fig. 4: DOC concentrations [µM C] in a cross-section of the Ob near Salekhard in June 2000.

3.2 Spatial distribution of DON

The major fraction of riverine nitrogen was organic. Dissolved inorganic nitrogen (nitrate, nitrite and ammonium) concentrations for surface samples were low, with a mean of 1.5 µM N (data not shown). DON values ranged between 5 and 15 µM N, with a mean of 8 µM N in the Kara Sea and a maximum of 15 µM in the Yenisei River (Table 1). These values agree well with mean concentrations of 13 µM N reported for the Lena and the Laptev Sea (5-6 µM N) by Lara et al. (1998) and Kattner et al. (1999), respectively. It is noteworthy that there is still some discrepancy in DON data reported for Arctic rivers and adjacent shelf seas. Values reported for the Lena by Cauwet and Sidorov (1996) were about three times higher than numbers reported by Lara et al. (1998). DON values reported for 8 rivers entering the Laptev- and East Siberian Seas averaged 26 µM N (Gordeev et al., 1996) also being significantly higher than what was reported by Lobbes et al. (2000). Whether these differences in DON concentrations are a result of strong seasonal DON variations (phytoplankton input) or due to different analytical methods still needs to be determined. In most cases DON is calculated as the difference between total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (nitrate, nitrite and ammonium). Holmes et al. (2001) pointed out problems with the long-term data set on DIN reported for Russian rivers. Similar problems might exist with respect to DON data. Hence, part of the observed discrepancy could stem from the diversity of methods, which were applied for the determination of DIN and DON in different studies. Independent determinations of organic nitrogen in ultrafiltered DOM (representing ca. 65% of total DOM) from Ob and Yenisei using a CHN-analyzer were consistent with the lower values of DON (Amon et al., unpublished data) reported here.

Table 1: Compilation of DON concentrations and C/N$_{(molar)}$ ratios for DOM in different aquatic environments of the Arctic.

	DON [µM N] mean (range)	C/N ratio mean (range)	Salinity range	Reference
Ob Estuary	10 (8-12)	35 (29-44)	13-20	this study [a]
Yenisei	13 (8-15)	42 (32-51)	0-19	this study [a]
Estuary	10	69	1.7	Lobbes et al. (2000)
Lena	33	23	0	Gordeev (1996)
	13 (9-28)	48 (30-58)	0	Lara et al. (1998)
	39 (6-48)	23 (20-53)	0-18	Cauwet and Sidorov (1996)
Kara Sea	8 (5-10)	26 (19-37)	21-28	this study [a]
Laptev Sea	5-6	18-25	30-34	Kattner et al. (1999)
Central Arctic	2-12 [b]	9-25 [c]	30-35	Wheeler et.al. (1997)

[a] surface samples of BP 00 cruise
[b] samples between 40 and 4000 m depth
[c] only samples from upper 100 m

3.3 Origin of DOM

C/N ratios are generally high in terrigenous DOM and low in marine DOM and represent a useful tracer to distinguish these two sources of DOM. Usually, C/N values for marine DOM range between 10 and 20 (Benner, 1998). Lara et al. (1998) reported C/N ratios between 10 and 25 for the Fram Strait region, and a mean C/N value of 13 was reported for Arctic Shelf seas by Wheeler et al. (1997). In this study we found relatively high values, even in the northernmost part of the Kara Sea, indicating the predominantly terrestrial nature of DOM in the entire Kara Sea. The C/N ratios of bulk DOM ranged from 19 to 51 (Table 1). Highest ratios were found in the Yenisei (up to 51), and lowest C/N ratios (19) were determined in the outer Kara Sea (Table 1). These values are in good agreement with the data reported by Lara et al. (1998) and Kattner et al. (1999) for the Lena and the adjacent Laptev Sea (Table 1). A strong terrigenous signal in Arctic shelf DOM was also reported by Kattner et al. (1999) who estimate that 60% of the total DOM in the Laptev Sea area have a terrigenous origin. Even in surface waters of the central Arctic Ocean (Opsahl et al., 1999) and in the East Greenland current (Opsahl et al., 1999; Amon, 2003) a clear signature of terrigenous DOM from Arctic rivers is evident. The C/N ratios between 29 and 51 in the estuaries of Ob and Yenisei indicated a predominantly terrestrial source for this material, with minor contribution of phytoplankton-derived material during the sampling period.

The higher DON concentrations reported in some of the recent literature (see above) resulted in much smaller C/N ratios. Cauwet and Sidorov (1996) report a mean C/N ratio of 23 for the Lena River (Table 1) and similarly low values (20.5 ± 2.6) were reported for several other Russian rivers by Gordeev et al. (1996) and Wheeler et al. (1997). The lower C/N ratios could indicate a larger contribution of phytoplankton-derived DOM during those studies. The here reported high C/N values for bulk DOM were confirmed by independent measurements of the C and N content of ultrafiltered and freeze dried DOM using a CHN-

analyzer. Considering that high molecular weight DOM and humic substances represent about 70% of total riverine DOM with C/N ratios between 34 and 50 (Thurman 1985; Amon unpublished data) the C/N values (> 30) reported here appear to be realistic for these estuaries. The dominance of terrestrially derived (allochthonous) DOC in the Kara Sea was also supported by low stable carbon isotope values, which were determined on ultrafiltered DOM. The $\delta^{13}C$ values of UDOM (>1 kDa) samples, taken during the BP-97 cruise in the estuaries of Ob and Yenisei ranged from -27.6 to -27.1 ‰ (Opsahl et al., 1999).

Excitation-emission matrix spectroscopy is another useful tool for identifying the sources of fluorogenic components of DOM in freshwater, estuarine and marine environments (e.g. Coble et al., 1993, Mopper and Schultz, 1993, Coble 1996; Del Castillo et al., 1999; Parlanti et. al., 2000; McKnight et al., 2001). Humic substances are a quantitatively dominating component of the dissolved organic carbon pool in the rivers Ob and Yenisei accounting for 60-75% of the dissolved organic carbon (data not shown). Since dissolved humic substances are also strong fluorophores, the measurement of fluorescence properties upon excitation with distinct wavelengths is an excellent means to analytically address a major part of riverine DOM.

Spectrally corrected excitation-emission contour plots of water samples from the rivers Yenisei and Ob are presented in Figure 5. The Yenisei is characterized by two distinct excitation/emission maxima (Ex_{max}/Em_{max}) at 270 nm/455 nm and 325 nm/443 nm, respectively (Fig. 5A). The corresponding maxima for the Ob are 270 nm/456 nm and 320 nm/438 nm, respectively (Fig. 5B). The occurrence of two distinct excitation/emmision peaks upon UV-excitation is a typical feature of riverine water (Coble, 1996; Del Castillo et al., 1999). Both peaks are generally referred to as humic-like fluorescence because their fluorescent signals are similar to those of humic substances extracted by XAD-resins from the same water samples (Coble 1996). The position of the fluorescence peaks of Yenisei and Ob (Ex_{max} = 325 nm and 320 nm, respectively) agrees well with the averaged Ex_{max}/Em_{max} of a variety of rivers (340 nm ± 10 nm/448 nm ± 6 nm) as reported by Coble (1996) suggesting that Arctic rivers are consistent with the observed fluorescence pattern of riverine DOM. The very similar Ex_{max}/Em_{max} of Ob and Yenisei indicate no substantial differences in the fluorophore composition of the DOM and thus the terrestrial source of the material. Hence, bulk fluorescence characteristics of the river endmembers are not an appropriate proxy to distinguish water bodies in the Kara-Sea with respect to their riverine source. However, the uniform and intense fluorescent signals of riverine DOM can be used to identify terrestrially-derived carbon in oceanic regions far away from its source thus providing an easy to measure parameter to assess the export of dissolved organic carbon from shelf areas to the open ocean (Amon, in press). The elevated fluorescence signals of the Yenisei as compared to the Ob reflect the higher DOC concentration of the Yenisei water sample (698 µM versus 519 µM in the Ob). Overall, the fluorescent intensity of the visible maxima in both rivers (43 and 39 QSU) exceed values reported by Coble (1996) for water samples from the Amazon Basin (20 QSU) and the Mississippi River (36 QSU) indicating a strong chromophoric component in the DOM of Yenisei and Ob.
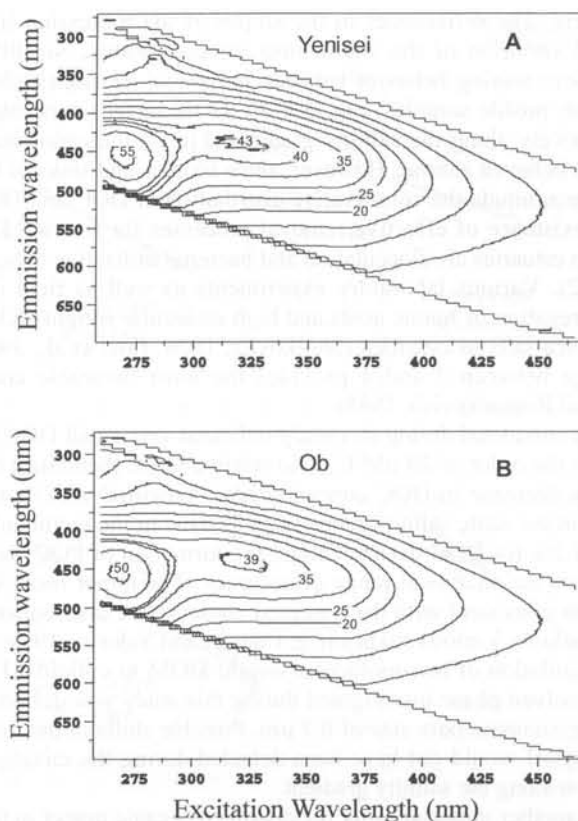
Fig. 5: Contour plots of fluorescence excitation emission matrices of two water samples from the rivers Yenisei (A) (salinity of 0.0, sampled 2000) and Ob (B) (salinity of 0.6, sampled 1999). Fluorescence signals were corrected for water Raman peaks and excitation/emission characteristics of the fluorometer. Isolines represent quinine sulfate units (1 QSU = 1 ppb quinine sulfate in 0.05 M sulfuric acid).

3.4 Behavior of DOM during estuarine mixing: potential sources and sinks

Due to the different catchment characteristics waters originating from the Yenisei contains higher silicate concentrations (~70 µM Si) than the Ob (~25 µM Si) and the marine samples in the Kara Sea (~15 µM Si). Based on these differences we used SiO_2 as a tracer to distinguish the relative contributions of the two rivers in the open Kara Sea as suggested by Stunzhas (1995). Thus, the mixing behavior of DOM along the salinity gradient could be investigated independently for both rivers.

The DOC versus salinity plots for both rivers showed that data over the entire salinity range fell close to the regression lines (Fig. 6 A-F) indicating the conservative distribution of riverine DOC in the Kara Sea. In general, a similar mixing pattern was observed during all

cruises and for both rivers. The differences in the slopes of the regression lines indicate interannual and seasonal variation of the endmember concentrations. No difference was observed in the conservative mixing behavior between horizontal mixing (surface samples) and vertical mixing (depth profile samples; Fig. 6 C-F). DON surface concentrations were also distributed conservatively along the salinity gradient (Fig. 7) indicating that dissolved carbon and nitrogen pools behaved similar. However, since sources and sinks of DOM on the shelf could be of similar magnitude the conservative distribution of DOC and DON does not necessarily exclude the existence of effective removal processes for riverine DOM. Major potential sinks of DOM in estuaries are flocculation and bacterial utilization (Thurman, 1985; Lee and Wakeham, 1992). Various laboratory experiments as well as field observations indicate the selective aggregation of humic acids and high molecular weight DOM under the flocculating influence of sea salts in estuaries (Sholkovitz, 1976; Ertel et al., 1986; Lisitzin, 1995). The salinity range between 2 and 4 provides the most favorable conditions for flocculation (Artemyev and Romankevich, 1988).

The mixing experiment conducted during this study indicated very small DOC losses in the low salinity range (<5) on the order of 20 µM C (3%) relative to the theoretical conservative mixing line (Fig. 8). This decrease in DOC concentrations coincided with increasing POC concentrations (7 µM C) in the same salinity range (Fig. 8). Due to the methodological error of about 5% for POC and 2% for DOC determination, the formation of POC and the loss of DOC were not much above the analytical range of accuracy. The minor loss (3%) of DOC during this experiment was consistent with the observed conservative distribution of riverine DOC along the salinity gradient. Various studies (e.g. Cauwet and Sidorov, 1996; van Heemst et al., 2000) reported coagulation of low-molecular weight DOM to colloidal DOM during estuarine mixing. The dissolved phase investigated during this study was defined by the use of GF/F filters with an approximate pore size of 0.7 µm. Possible shifts in the molecular size distribution below this cut-off would not have been detected during the mixing experiment nor in the DOC distribution along the salinity gradient.

Bacterial utilization is another important sink for dissolved organic matter in the estuaries. Results of a long-term degradation experiment (Fig. 9) revealed only minor losses of DOM (ca. 30 µM C or 4.5%) over a 21 month incubation period. The fact that we could not detect DOC losses in the first two weeks of the experiment indicated the absence of labile compounds in the freshwater endmember. Concentrations of inorganic nutrients were low (0.1 µM phosphate and 0.8 µM DIN) potentially limiting the degradation of a major portion of riverine DOM, however, they should have been enough to readily degrade at least 20-30 µM DOC. We believe that bacterial consumption of Yenisei DOM was limited by the refractory nature of DOM rather than by nutrient limitation of the bacterial community.
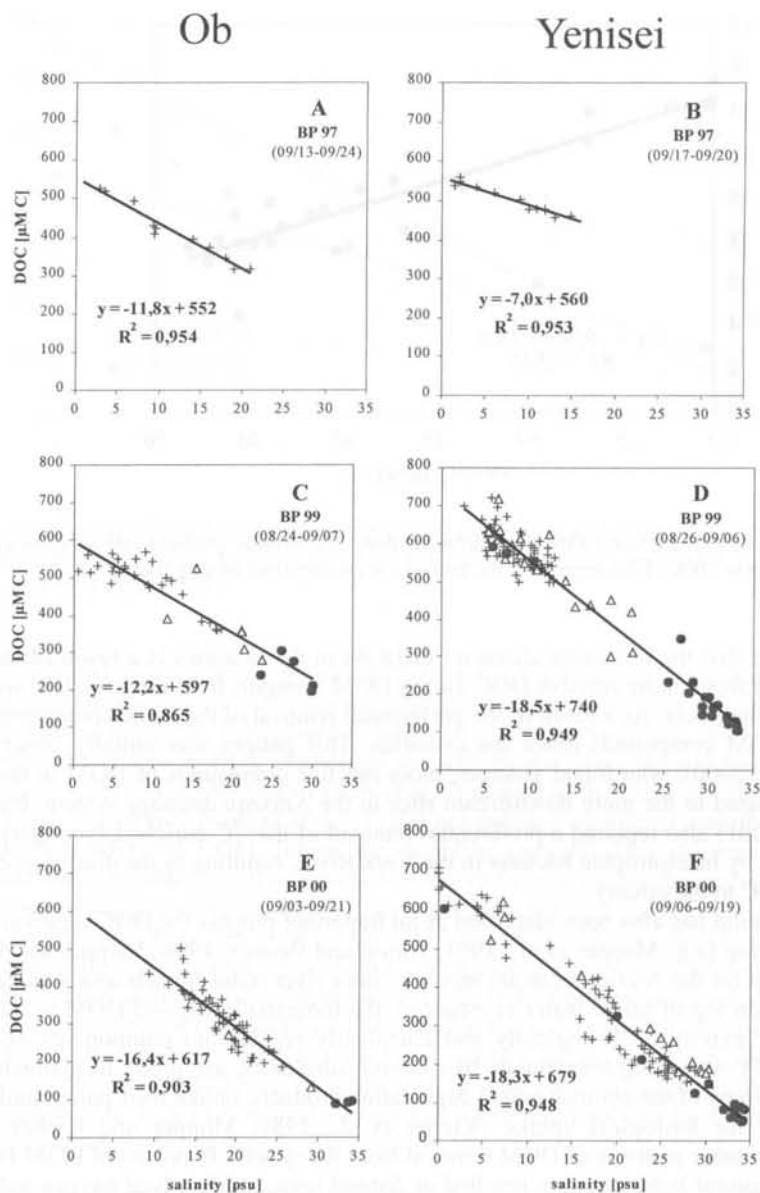
Fig. 6: DOC distribution along the salinity gradient in the Ob (A,C,E) and Yenisei Estuary (B,D,F). Samples are subdivided into surface samples (+) pycnocline samples (Δ) and deep samples (●).
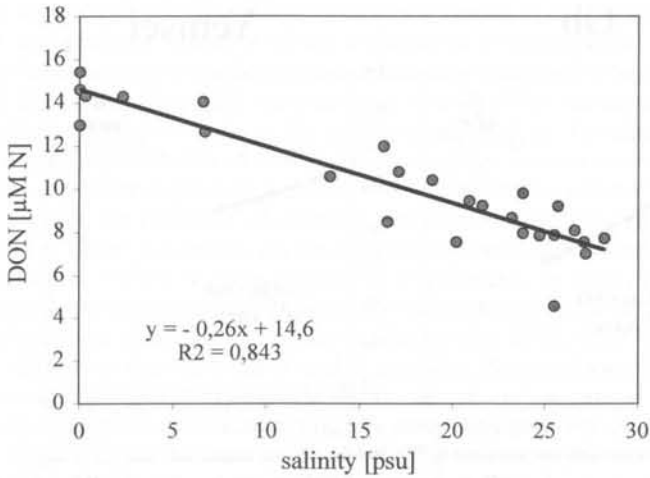
Fig. 7: Distribution of surface DON concentration along the salinity gradient (all samples collected during the cruise in 2000). Line represents the theoretical conservative mixing line.

We suggest that the refractory character of DOM in the estuaries is a result of the rapid degradation of fresh, more reactive DOC during DOM transport from the terrestrial source to the mouth of the rivers. As a result of the preferential removal of the labile components, only refractory DOM compounds reach the estuaries. This pattern was initially observed by Hedges et al. (2000), who found younger, more reactive compounds of DOM in the upper reaches compared to the more downstream sites in the Amazon drainage system. Raymond and Bauer (2001) also reported a preferential removal of the ^{14}C-enriched (younger), labile DOC fraction by heterotrophic bacteria in the York River, resulting in the discharge of more refractory DOC to the estuary.

Photooxidation has also been identified as an important process for DOC removal during estuarine mixing (e.g. Mopper et al., 1991; Amon and Benner, 1996; Mopper and Kieber, 2000), but data for the Arctic Ocean are missing. Since river water spreads as a relatively thin surface layer on top of saline water in estuaries, the terrestrially-derived DOM is subject to enhanced UV-exposure. Biologically and chemically recalcitrant components of DOM, particularly UV-absorbing compounds like humic substances, are prone to photochemical degradation. Some of the photochemical degradation products, unlike their parent molecules, are available for biological uptake (Kieber et al., 1989; Mopper and Kieber, 2000) representing another pathway of DOM removal from the system. Exposure of DOM from the Yenisei to a natural light spectrum resulted in distinct losses of dissolved oxygen indicating the potential photoreactivity of Arctic river DOM (Meon and Köhler, 2002). However, due to the strong light attenuation in the Kara Sea water column (Burenkov et al., 1995) photochemical oxidation is restricted to the uppermost layer of the estuary, affecting only a small portion on a volume basis.
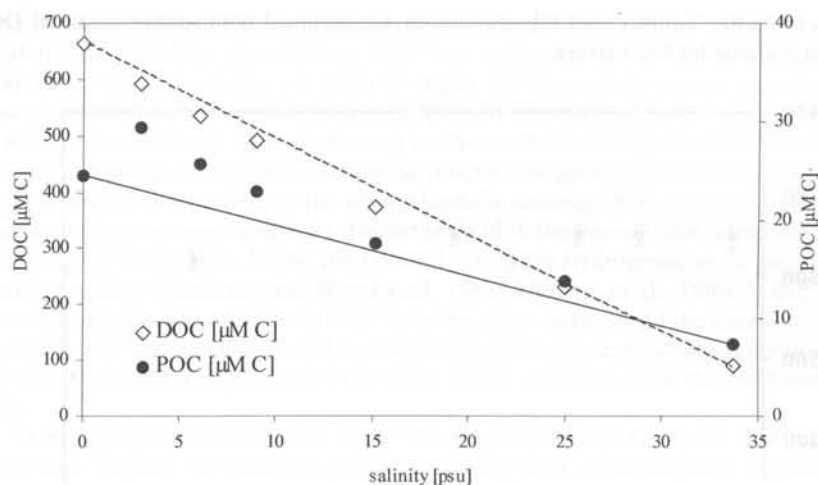
Fig. 8: Partitioning of DOC and POC during mixing experiment of Yenisei water (salinity of 0) and open Kara Sea deep water (salinity of >33). The two endmembers and the 5 mixtures are each represented by one pair of data.

An important autochthonous source of DOC on the Kara Sea shelf is primary production. Recent estimates of the annual primary production in the Kara Sea are around 20 Tg C (Vinogradov et al., 2001; Romankevich and Vetrov, 2001; Sakshaug, 2003). This is more than twice the amount of DOC discharged annually by the rivers Ob and Yenisei. However, the largely conservative behavior of DON (Fig. 7) as well as the relatively high C/N ratios in DOM along the salinity gradient (Fig. 10) did not indicate significant contributions of fresh phytoplankton-derived DOM during the sampling periods. This is consistent with the moderate levels of chlorophyll-a observed in the study area during the cruises (Nöthig, this volume). Typically, surface chlorophyll-a ranged from 0.5 to 5 µg Chl-a l^{-1}, with very low values in the open Kara Sea north of 76°N (Nöthig, this volume). Additionally, bacterial utilization of fresh phytoplankton-derived DOM has been shown to be very efficient (Amon et al., 2001) representing another explanation for the lack of phytoplankton-derived DOM and the dominance of terrestrially-derived DOM during the late summer-fall period in the study area. Overall, the absence of major sources and sinks on the shelf confirms the conservative behavior of riverine DOC during estuarine mixing. The observed scatter in the DOC versus salinity plots (Fig. 6 A-F) was likely a result of the strong temporal DOC variations of the riverine endmember during the sampling periods.

3.5 Seasonal aspects of riverine DOC concentrations

Up to now information on seasonal DOC dynamics in Ob and Yenisei is missing. Cauwet and Sidorov (1996) presented TOC concentrations over an entire annual cycle for the Lena River and this is to our knowledge the only study that contains data with seasonal resolution for large Arctic rivers. Cauwet and Sidorov (1996) reported maximum TOC concentrations (> 900 µM) during the peak flood and winter values as low as 300 µM TOC. Since the

hydrographs of Lena, Yenisei, and Ob are similar we assumed comparable seasonal DOC concentration patterns for the 3 rivers.
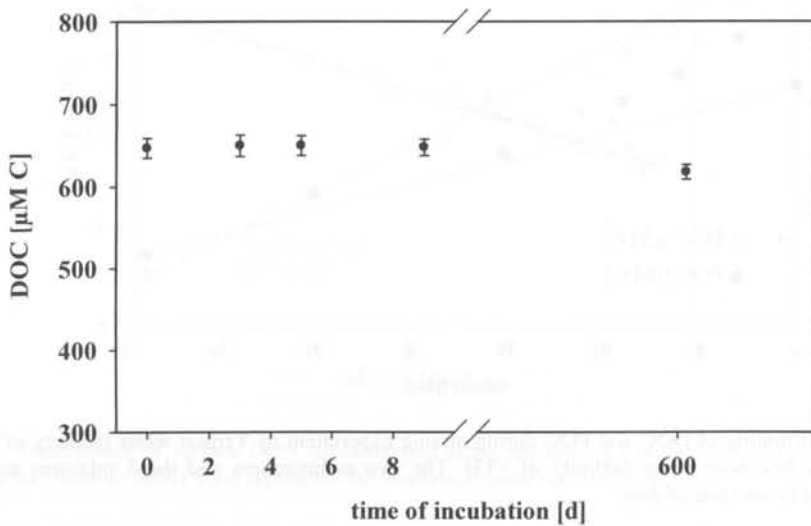

Fig. 9: Bulk DOC concentration (incl. standard deviation) of Yenisei River water during a bacterial decomposition experiment.
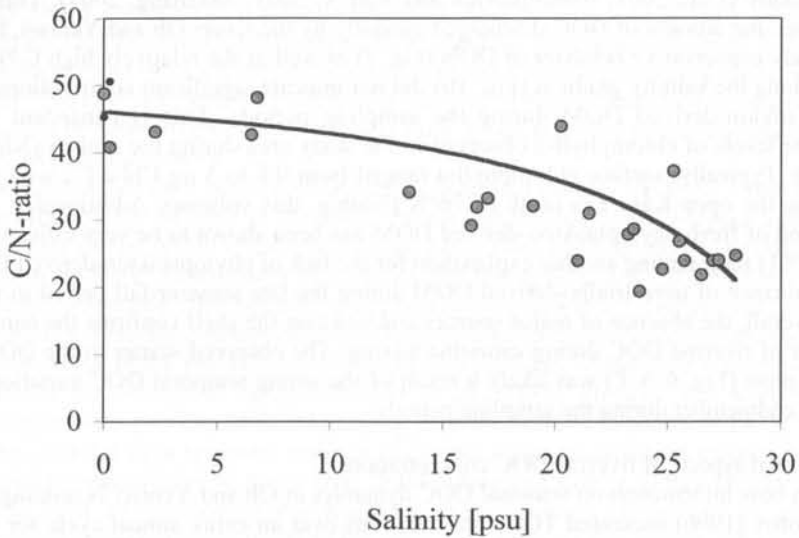

Fig. 10: Distribution of C/N ratios along the salinity gradient (all samples collected during the cruise in 2000). Line represents the theoretical conservative mixing line.

Annual minimum DOC concentrations (~300 µM C) occur in winter when rivers are predominantly fed by groundwater with low carbon content. During the spring flood in May/June, when the rivers are predominantly fed by surface runoff and interflow, DOC concentrations reach maximum values (> 900 µM C). Organic matter appears to accumulate in soils of the extended watersheds over the 8-month low flow period between late summer and the following spring flood. During the onset of the spring flood some of the accumulated organic matter is exported to the river channels causing DOC concentrations to increase sharply with increasing freshwater discharge. Within this period DOC concentrations usually reach higher values than during the falling limb of the hydrograph at the same water stage. Various studies (Mantoura and Woodward, 1983; McLean et al., 1999; Schiff et al., 1999) reported such flushing effects for DOC after baseflow periods of long duration. Accordingly, the DOC concentration of 939 µM C determined in the Ob near Salekhard about 3 weeks after the flood maximum might have even been higher shortly before the freshwater discharge peak.

To gain a better understanding of the temporal variations of riverine DOC concentrations in Ob and Yenisei, we used the theoretical endmember concentrations calculated from the linear regressions presented in Figure 6 A-F. We combined theses values with actual measurements at zero salinity collected during our study or by other investigators and plotted them against the sampling date (Fig. 11). The resulting concentration pattern clearly indicates decreasing DOC concentrations during the post peak flow season. The relatively low DOC concentration in the Ob endmember in 1999 might be a result of the exceptionally high discharge of long duration during this year (Fig. 1).
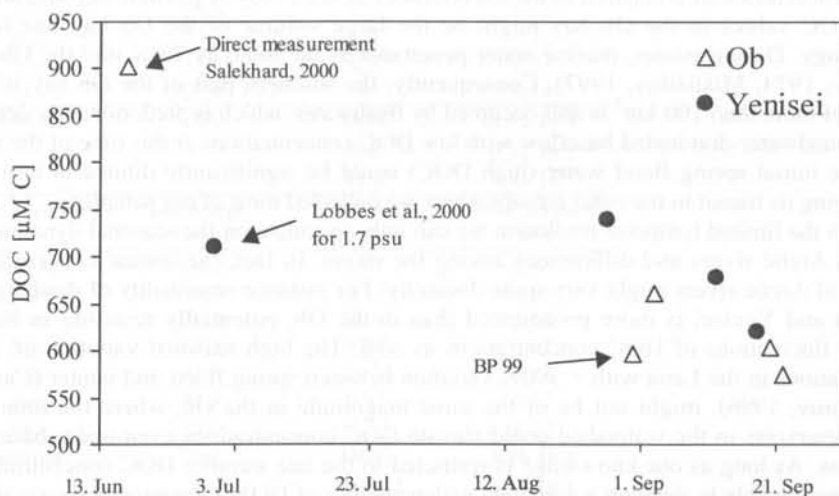

Fig. 11: Estimated seasonal distribution of DOC endmember concentrations. Theoretical endmember concentrations were calculated from the regression lines in Figure 6. These values were assigned to the sampling date, when the lowest salinity was observed. The Ob dataset for the BP 2000 cruise was subdivided into an early and late sampling period.

To match discharge data, which are monitored at Salekhard and Igarka, respectively (Fig. 1), with the observed concentrations in the estuaries, one has to consider the different morphology of the two estuaries. Due to a significantly wider river basin the Ob has a slower current with several months of passage time in the Ob bay during the peak flow period (Harms, pers. comm.). In contrast, the water flow in the relatively narrow Yenisei delta is much faster (Lein et al., 1996). Consequently, a fresh water lens, which is sampled during late August or early September near 73°N in the Ob Estuary may originate from the peak flow period, whereas water sampled in the Yenisei Estuary at the same latitude and time stems predominantly from the post peak flow season.

Following the logic of increasing DOC concentrations with increasing freshwater discharge one would expect DOC concentrations to be higher in the Ob relative to the Yenisei Estuary. However, all theoretical endmember concentrations determined from the estuaries in the Ob are clearly lower than in the Yenisei and much lower than the direct measurement near Salekhard (Figs. 6 and 11). Ludwig and Probst (1996) established empirical relationships between organic carbon fluxes and various factors characterizing the catchment basins of major world rivers. According to their model DOC concentrations increase with flatter morphologies and larger carbon reservoirs in the soils of the drainage basins, also suggesting higher DOC concentrations for the Ob than for the Yenisei. In fact, one recent study did report higher DOC concentrations for the Ob bay (600-830 μM) relative to the Yenisei (300-350 μM) during the Dimitry Mendeleev expedition in August-October 1993 (Dai and Martin, 1995; Gordeev, 1999). A dilution effect due to the inflow of Taz and Pur into the Ob bay is unlikely since together both rivers annually contribute only about 15% to the total volume flux entering the Ob bay (Pavlov and Pfirman, 1995) and, as shown for the Pur, hardly differ in TOC concentrations compared to the Ob (Gordeev et al., 1996). A possible explanation for lower DOC values in the Ob bay might be the large volume of the Ob bay due to its morphology. During winter, marine water penetrates as far south as 70°N into the Ob bay (Vasiliev, 1974; Mikhailov, 1997). Consequently, the southern part of the Ob bay with a volume of more than 100 km^3 is still occupied by freshwater, which is predominantly derived from groundwater-dominated baseflow with low DOC concentrations at this time of the year. Thus, the initial spring flood water (high DOC) could be significantly diluted in terms of DOC during its transit to the outer estuary where we collected most of our samples.

Due to the limited temporal resolution we can only speculate on the seasonal dynamics of DOM in Arctic rivers and differences among the rivers. In fact, the annual concentration patterns of Arctic rivers might vary quite distinctly. For instance seasonality of discharge in the Lena and Yenisei is more pronounced than in the Ob, potentially resulting in higher seasonal fluctuations of DOC concentrations as well. The high seasonal variation of TOC concentrations in the Lena with > 300% variation between spring flood and winter (Cauwet and Sidorov, 1996), might not be of the same magnitude in the Ob, where the immense carbon reservoirs in the watershed could elevate DOC concentrations even under baseflow conditions. As long as our knowledge is restricted to the late summer DOC concentrations, we will not be able to develop a complete understanding of DOM dynamics in Arctic rivers and how they are linked to the hydrograph, catchment morphology, and organic carbon reservoirs in the watersheds.

3.6 Assessment of riverine DOC fluxes into the Kara Sea

Most studies, which report annual carbon fluxes from Arctic rivers assume a mean annual discharge and TOC concentration. TOC concentrations are usually determined in late

summer, when ice conditions allow sampling in the estuaries. This approach largely ignores the strong seasonal variability of freshwater discharge and TOC concentrations. The data of Cauwet and Sidorov (1996) for the Lena River are a notable exception and show that the annual variations of TOC concentrations are positively correlated with water discharge. Thus, seasonal resolution of TOC concentration is essential for meaningful flux estimates. To account for the observed seasonal variation we estimated annual DOC fluxes for Ob and Yenisei by multiplying the multiyear monthly average water discharge for the period 1980-1999 with measured and estimated mean DOC concentrations of the corresponding months. Due to the lack of seasonal resolution in our DOC data set we estimated missing values using information from other studies. These estimates are based on typical annual concentration patterns reported for Arctic rivers by Cauwet and Sidorov (1996). The summer period (June-September), which accounts for about 70% of the total organic carbon discharged in Ob and Yenisei is covered well by our own data set. The winter (November-April) and preflood DOC values were adopted from Cauwet and Sidorov (1996). From the monthly resolved data (Table 2) we calculated the weighted annual DOC concentrations to be 681 µM C for the Yenisei and 640 µM C for the Ob.

Table 2: DOC and TOC flux estimates for the rivers Ob and Yenisei.

Ob	Discharge [i] [km]	DOC [mgL^{-1}]	DOC export [10^{6}t]
Nov.-Apr.	82,8	3,6 [a]	0,30
Mai	39,5	9,0 [b]	0,36
June	90,4	10,8 [c]	0,98
July	79,6	9,0 [c]	0,72
Aug	53,5	7,7 [c]	0,41
Sep	32,4	6,5 [f]	0,21
Oct	27,9	5 [b]	0,14
annual	**406**	**DOC**	**3,12 10^{6}t**
		POC [g]	**0,31 10^{6}t**
		TOC	**3,43 10^{6}t**
Yenisei	Discharge [i] [km]	DOC [mgL^{-1}]	DOC export [10^{6}t]
Nov.-Apr.	132,5	3,6 [a]	0,48
Mai	77,4	8,5 [b]	0,66
June	201,8	10,8 [d]	2,18
July	64,3	9,6 [d]	0,62
Aug	41,9	9 [d]	0,38
Sep	41,3	8,3 [c]	0,34
Oct	34,9	5,7 [b]	0,20
annual	**594**	**DOC**	**4,86 10^{6}t**
		POC [h]	**0,17 10^{6}t**
		TOC	**5,03 10^{6}t**

[a] adopted from Cauwet and Sidorov (1996), [b] estimated, based on Cauwet and Sidorov (1996), [c] direct measurement, [d] estimated, based on Ob data and theoretical endmember concentrations, [e] derived by interpolation, [f] estimated, based on theoretical endmember concentrations, [g] annual POC flux calculated from POC/DOC ratio (Nestorova, 1960), [h] annual POC flux from Lobbes et al. (2000), [i] Discharge data are based on monthly mean values for the Stations Salekhard (Ob) and Igarka (Yenisei) in the period 1980-1999.

For easier comparison of carbon fluxes with existing studies we included TOC estimates in Table 2, assuming a DOC/TOC ratio of 0.91 (Nesterova, 1960). This relation is in good agreement with recent studies from other Siberian rivers (Opsahl et al.,1999; Lobbes et al., 2000; Romankevich et al., 2000). Our annual TOC flux estimates are $3.43 \ 10^{12}$ g yr^{-1} for the Ob and $5.03 \ 10^{12}$ g yr^{-1} for the Yenisei (Table 2). The estimated TOC flux for the Yenisei agree well with the value reported by Lobbes et al. (2000; $5.03 \ 10^{12}$ g yr^{-1}), while other studies like Gordeev et al.(1996; $4.59 \ 10^{12}$ g yr^{-1}) or Telang et al. (1991; $4.13 \ 10^{12}$ g yr^{-1}) reported somewhat lower values. Previous TOC flux estimates for the Ob range between $3.05 \ 10^{12}$ g yr^{-1} (Gordeev et al., 1996) and $3.69 \ 10^{12}$ g yr^{-1} (Romankevich and Artemyev, 1985). Since long term discharge data are relatively robust, different estimates of TOC fluxes are mainly due to uncertainties in the seasonal variation of TOC concentrations. Several studies that presented TOC flux estimates (Telang, 1991; Gordeev et al., 1996; Ludwig and Probst, 1996) refer to data presented by Romankevich and Artemyev (1985), which themselves are based on data from Nesterova (1960) and Maltseva (1980). Hence, the majority of existing flux estimates appears to be based on only very few single point measurements. Some of the differences in flux estimates occur because some export rates are related to the most downstream discharge monitoring stations at Salekhard and Igarka (Lobbes et al., 2000) while other studies (Gordeev et al., 1996) calculate carbon fluxes for the entire catchment by extrapolation. Another problem might be that discharge and TOC were often not determined at the same location. Some studies (this study for the Yenisei; Lobbes et al., 2000) determined fluxes by multiplying concentrations observed in the estuary with discharge data that were monitored some hundreds of kilometers south, whereas other studies (this study for the Ob; Gordeev and Tsirkunov, 1998 for the Ob) determined organic carbon concentrations directly at the station, where the discharge is monitored. The latter is the proper way to do it, but often difficult to accomplish at such remote locations. Additional uncertainties are due to the differences in the applied analytical techniques, which make a comparison of the available data difficult. Many of the existing investigations are based on TOC concentration data determined on unfiltered river waters by wet oxidation (Romankevich and Artemyev, 1985), whereas other studies (this study, Lobbes et al., 2000) determined POC and DOC independently, using high temperature catalytic combustion. With all these uncertainties it is surprising how similar the older TOC flux estimates are to the estimates of this study, which considers the seasonal variation of discharge and DOC.

Clearly more work remains to be done to fully resolve seasonal patterns of DOC in large Arctic rivers and to confirm current TOC fluxes from the carbon rich northern latitude watersheds to the Arctic Ocean. In order to evaluate anthropogenic effects on the Arctic carbon cycle in the future, it is essential to create a reliable baseline for seasonal carbon fluxes under current conditions (Holmes, et al., 2000). Several studies indicate that carbon fluxes in Siberian rivers are not constant. Maltseva et al. (1980) and Romankevich and Artemyev (1985) report declining TOC fluxes within the last decades as a result of changes in land use. Effects of hydraulic engineering, particularly in the Yenisei, also influence the hydrologic regime and carbon fluxes (Shiklomanov et al., 2000). Climate change related alterations in the soil water regime of the Kara Sea drainage basin have recently been indicated by Savelieva and Semiletov (2001). Vörösmarty et al. (2001) reported increases in the baseflow of the Yenisei coupled to reductions in permafrost. As long as carbon flux data for large rivers like Ob and Yenisei are incomplete, linkages between the terrestrial and oceanic carbon pools in the Arctic will remain elusive. Numerical models for the prediction of changes in the Arctic

system will require reliable data on carbon transport from terrestrial ecosystems to the Arctic Ocean. A seasonally resolved determination of organic carbon concentrations and fluxes at the stations, where discharge is monitored would be most appropriate to overcome the current gap.

Acknowledgements

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