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Particulate matter fluxes in the southern and central Kara Sea compared to sediments: Bulk fluxes, amino acids, stable carbon and nitrogen isotopes, sterols and fatty acids

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Abstract

The Kara Sea is one of the arctic marginal seas strongly influenced by fresh water and river suspension. The highly seasonal discharge by the two major rivers Yenisei and Ob induces seasonal changes in hydrography, sea surface temperature, ice cover, primary production and sedimentation. In order to obtain a seasonal pattern of sedimentation in the Kara Sea, sediment traps were deployed near the river mouth of the Yenisei (Yen) as well as in the central Kara Sea (Kara) within the framework of the German–Russian project "Siberian River run-off; SIRRO". Two and a half years of time-series flux data were obtained between September 2000 and April 2003 and were analyzed for bulk components, amino acids, stable carbon and nitrogen isotopes as well as sterols and fatty acids.

Sediment trap data show that much of the annual deposition occurred under ice cover, possibly enhanced by zooplanktonic activity and sediment resuspension. An early bloom of ice-associated algae in April/May occurred in the polynya area and may have been very important to sustain the life cycles of higher organisms after the light limitation of the winter months due to no/low insolation and ice cover. The strong river input dominated the months June–August in the southern part of the Kara Sea. The central Kara Sea had a much shorter productive period starting in August and was less affected by the river plumes. Despite different time-scales of sampling and trapping biases, total annual fluxes from traps were in the same order of magnitude as accumulation rates in surface sediments. Terrestrial organic carbon accumulation decreased from 10.7 to $0.3\,g\,C\,m^{-2}\,a^{-1}$ from the riverine source to the central Kara Sea. Parallel to this, preservation of marine organic matter decreased from 10% to 2% of primary productivity which was probably related to decreasing rates of sedimentation.

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1. Introduction

About 10% of the global freshwater discharge occurs in the Arctic Ocean (Aagaard, 1994). More than one-third of it is discharged into the Kara Sea (Fig. 1), mainly via the Yenisei and Ob, the second and third largest arctic rivers transporting annually about 1000 km^{-3} water (Milliman and Meade, 1983; Telang et al., 1991). The associated supply of more than 22×10^6 t a^{-1} of sediment, estimated at the northernmost gauging stations is small compared to rivers of similar size from lower latitudes (Milliman and Meade, 1983). Low total suspended matter (TSM) concentrations in addition to low concentrations of the dissolved fraction are due to arctic climate and the related limited vegetation and land use in the catchment (Holmes et al., 2002). Change in land use and global warming have recently increased nutrient concentrations and water discharge in arctic rivers (Peterson et al., 2002). Partial melting of the permafrost soils may further increase nutrient and suspended matter concentrations in the near future (Syvitski, 2002) leading to enhanced productivity in the arctic coastal seas also stimulated by longer ice-free periods.

It was one of the aims of the multidisciplinary Russian–German research project "Siberian River run-off (SIRRO)" to understand the role of river supply for the recent sedimentation processes in the Kara Sea (Stein et al., 2003). Sediment traps were deployed in order to obtain information about processes taking place during the winter and spring season when ice cover or ice melt make the area difficult to access. The data presented here are the first seasonal particle flux data of high resolution from the southern and central Kara Sea and provide three records of seasonal changes in vertical fluxes to its deep saline water layer.

2. Materials and methods

2.1. Study area

Hydrography of the Kara Sea has a climatically induced high seasonality. The southern Kara Sea is ice free only from mid-July to mid-October (Pavlov and Pfirman, 1995) (www.aari.nw.ru). The central and northern Kara Sea remain ice covered until the end of August in most years. Maximum river discharge occurs in June (Fig. 2a), both, on and under the ice with the peak being more pronounced in the Yenisei than in the Ob (Meade et al., 2000). The high discharge period is characterised by strong stratification with warmer and less saline surface water and a deep salt wedge intruding into the estuaries (Harms et al., 2003). The thermohalocline separating surface and deep water masses is situated at about 6–8 m in the inner Kara Sea and can be at 20 m water depth in the offshore areas (Pavlov and Pfirman, 1995; Shmelkov et al., 2002). In summer the average salinity is around 10 in the surface waters of the estuaries and increases to >30 in the northern Kara Sea (Fig. 1) whereas in winter the river plume water mass is restricted to a narrow belt along the coast line (Pivovarov et al., 2003).

Long-term records of freshwater and suspended matter discharges are available from several hydrographic stations along both rivers (Bobrovitskaya et al., 1997; Meade et al., 2000; Holmes et al., 2001). TSM supply to the Kara Sea after dam constructions in the upper reaches of the rivers was estimated as 4.2×10^6 t a^{-1} at Igarka for the Yenisei
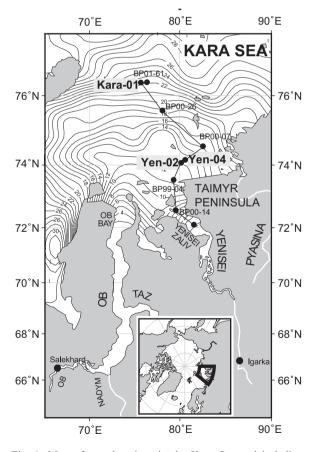

Fig. 1. Map of trap locations in the Kara Sea and isohalines (in psu) of compiled summer salinities (Dmitrenko et al., 1999). Kara-01: Kara Sea 01; Yen-2, Yen-04: Yenisei 02 and 04.

Fig. 2. Water discharge by the Ob at Salekhard and by the Yenisei at Igarka (a) insolation at the Yenisei and Kara trap locations (b) total particle fluxes measured by sediment traps (c) weekly averages of current speeds in cm/s measured by current meters deployed at 55 m at the Kara Sea and at 21 and 30 m, respectively, at the Yenisei location (d). Note the different dates on the *x*-axis.

and 16.2×10^6 t a^{-1} at Salekhard for the Ob (Bobrovitskaya et al., 1996). Both northernmost gauging stations are about 600 km south of the rivers mouths (Fig. 1). A recent calculation of TSM and particulate organic carbon (POC) fluxes at the river mouths suggests a TSM discharge by the Yenisei (5×10^6 t sediment a^{-1}) comparable to the above earlier estimate from Igarka indicating that the lower Yenisei is mainly a by-pass system (Gebhardt et al., 2004). The Ob discharge reaching the Kara Sea (3.76×10^6 t a^{-1}) appears to be only about one-fourth of the amount discharged at Salekhard, which may be due to deposition in the Ob Bay (Gebhardt et al., 2004). Flood events occurring about every 10 years (Bobrovitskaya et al., 1996) may, however, periodically transport this material to the Kara Sea (Gebhardt et al., 2004). Most of the TSM and organic matter reaching the Kara Sea is deposited as a thick sediment package extending from the estuaries to

about 74°N (Dittmers et al., 2003). This region was named the "marginal filter" as flocculation and deposition may remove most of the river contaminants from the water column and thus prevent their export to the central Arctic Ocean (Lisitzyn, 1995). Several studies based on stable isotopes and biomarkers showed that most organic matter preserved in the sediments of the southern Kara Sea was of terrestrial origin (Fahl et al., 2003; Fernandes and Sicre, 1999; Krishnamurthy et al., 2001). These findings are similar to those on other Arctic shelves such as the Beaufort Sea (Goni et al., 2005).

Enhanced primary productivity is mainly restricted to the short ice-free period in late summer or may take place in the polynya area (Wassmann et al., 2004) which is situated in the southern Kara Sea north of the fast ice zone (Harms et al., 2000). Primary productivity can attain rates of more than 200 mg C m^{-2} d^{-1} north of the areas of high

turbidity from river suspension (Vedernikov et al., 1995; Vinogradov et al., 2000). Timing of ice break up and ice drift varies interannually and is largely controlled by winds that together with seasonal river discharge make the whole Arctic a region of very patchy and variable primary production and POC export during the season of sufficient light and ice-free conditions (Wassmann et al., 2004). Vinogradov et al. (2000) estimated a total primary production of $20 \times 10^6\,t\,C\,a^{-1}$ for the entire Kara Sea. Nöthig et al. (2003) and Deubel et al. (2003) found large interannual differences not only in total biomass but also in spatial distribution and composition of phyto- and zooplanktonic communities in the Kara Sea—evidently driven by the timing and amount of river run-off. Short-term trap deployments showed that plankton blooms with very high fluxes of fresh organic matter can occur off the river mouths in late summer when river discharge is reduced (Gaye-Haake et al., 2003; Hirche et al., 2006).

The processes described above result in a complex structure and variable distribution of water masses in the Kara Sea characterised by different temperatures, nutrient and oxygen concentrations (Pivovarov et al., 2003). Sedimentation processes in the Kara Sea can, therefore be expected to be very complex and variable depending on river discharge, ice conditions, water mass distribution and circulation.

2.2. Sampling

Samples were obtained at a southern (Yen) and northern (Kara) location (Fig. 1) using two cylindrical sediment traps (Hydrobios, Kiel, Germany, http://www.hydrobios.de) equipped with, respectively 24 and 12 collection cups. The height of the collecting cylinder is 90 cm, the diameter of its opening area is 14 cm. Sampling intervals varied from 6.5 to 56 days according to the expected variations in particle fluxes in order to collect material sufficient for analyzes. The Yen 02 trap was deployed from September 2000 to August 2001 at a depth of 20 m at $74°\,00.28'$N, $80°00.45'$ E; total water depth was 31 m. The Kara 01 trap was deployed from September 2001 to August 2002 at $76°12.08'$N, $75°45.3'$E at a water depth of 54 m. Total water depth was 73 m at this location. A second trap system moored at the Yen site (Yen 03) did not collect samples due to water inflow into the electronic housing. The Yen 04 deployment ($74°00.1145'$N; $80°19.4613'$E) had a trap depth of

29 m and a total water depth of 40 m and collected 10 samples from October 2002 to April 2003 until water flowed into the electronic housing and stopped further sampling. Aanderaa current meters RCM 9 were deployed at trap depths from September 2001 to April 2002 at the Yen and Kara stations (Yen 03, Kara 01) and from October 2002 to April 2003 at the Yen station (Yen 04).

After recovery trap samples were immediately cooled at $4\,°C$ until further processing. Before splitting into aliquots by a rotary splitter, swimmers were picked out. Aliquots for geochemical analyses were filtered on preweighed polycarbonate filters ($0.45\,\mu m$) and dried at $40\,°C$. For analyses samples were removed from the filters and ground in an agate mortar. Yen 02 samples number 7–18 were filtered on GFF filters of which small portions were cut out and used for analyses. Biogenic Opal could not be determined on these samples

2.3. Methodological limitations of sediment trap experiments

Trapping efficiencies depend on sediment trap geometry, current speeds, particle size and tilt of traps (Gardner, 1999; Gust et al., 1992; Gust and Kozerski, 2000). Generally, cylindrical traps seem to collect more material with increasing current speeds (Gust et al., 1996). Flux amounts are also affected by active swimmers which die from the trap poison and add to the material caught in traps (Lee et al., 1988, 2000). Furthermore, the solubilization of collected particles in sampling cups strongly affects shallow traps (Antia, 2005). Solubilization within the first few days of storage in the sampling cups may reduce carbon as well as other biogenic element fluxes considerably (Kähler and Bauerfeind, 2001). This may not only change the quantity but also the quality of fluxes (Antia, 2005). Kähler and Bauerfeind (2001) did, however, not find an effect on the seasonality of fluxes and composition as recorded in traps suggesting that the solubilization takes place immediately and is insignificant after the first few days. Except for a careful picking of swimmers from trap samples we did not correct for these biases but evaluate them in the discussion.

2.4. Analytical procedures

2.4.1. Bulk components
Total carbon and nitrogen were measured by a flash combustion CNS Carlo Erba 1500 analyzer

(Erba Science, Milan, Italy). The precision of this method is 0.15% for carbon and 0.005% for nitrogen. C/N-ratios were calculated on a molar basis. Carbonate percentages were determined by a Wösthoff Carmhograph 6 (Bochum, Germany) of all suspended matter samples from 1999, all sediment samples from 1997 and all trap samples as well as selected sediment and suspended matters samples from the subsequent sampling campaigns. The standard deviation of results is 1%. All carbonate measurements were below 0.2%. As this is very close to the detection limit we further assumed that total carbon equals organic carbon. Biogenic opal was determined photometrically in a modified version of the method of Mortlock and Froehlich (1989). All bulk components are presented as weight%.

2.4.2. Amino acids (AA) and hexosamines

Total hydrolysable AA were analyzed with a Pharmacia LKB Alpha Plus 4151 AA Analyzer (Freiburg, Germany). After hydrolysis of 30–40 mg for sediments and 2–4 mg for sediment trap material with 6 N HCl for 22 h at 110 °C an aliquot of the hydrolyzed sample was evaporated to dryness in a rotary evaporator. To remove acid the sample was taken up in deionised water three times and evaporated to dryness. The sample was then taken up in a citrate buffer of which 50 µl were injected into the Amino Acid Analyzer. Separation was carried out by a cation exchange resin (type 475–6 µm) from which the momomers were eluted with citrate buffers of different concentrations, pH and at different temperatures. After elution a reagent containing phthaldialdehyde was added which reacted with amino acids forming a fluorescent complex. Fluorescence intensity was measured with a Shimadzu FLD-6A fluorescence detector (excitation wavelength: 350 nm; fluorescent wavelength: 450 nm). AA concentrations were quantified by comparison with an AA standard (SIGMA AA-S-18) which was run after every eighth sample. Duplicate analysis resulted in a relative error of 4% for total AA.

In addition to the total concentrations specific AA ratios were used as indicators of organic matter degradation intensity. The ratio of the aromatic AA tyrosine and phenylalanine to the non-protein amino acids β-alanine and γ-aminobutyric acid (RI; Jennerjahn and Ittekkot, 1999) is higher when organic matter is fresher as the aromatic AA are among the most labile whereas the latter are the

most stable AA. Similarly, the ratio of aspartic acid to ß-alanine was often used to determine the relative state of degradation as the latter is probably the degradation product of aspartic acid or may not be taken up by organisms as it is not among the essential AA (Ittekkot et al., 1984; Lee, 1988; Lee and Cronin, 1982, 1984).

The molar percentages of the 14 protein AA were used to calculate the degradation index (DI) developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999) which assesses the diagenetic alteration of a sample by comparing it to a set of 28 samples of different degradation states and environments. Molar percentages of individual AA are standardised by the mean and standard deviations of the 28-sample data set. The DI then integrates the AA weighed by the factor coefficients for the first axis of the principal component analyses (PCA) of Dauwe et al. (1999) according to the formula:

$$ DI = \sum_i \left[\frac{var_i - AVGvar_i}{STDvar_i} \right] fac.coef._i, $$

where var_i is the original mole percentage of each AA_i, $AVGvar_i$ and $STDvar_i$ are the mean and standard deviations and $fac.coef._i$ is the factor coefficient of the first axis of the PCA of Dauwe et al. (1999). The DI thus represents the cumulative deviation with respect to an assumed average molar composition with negative values indicating more and positive values less degradation than the average.

The DI of Dauwe et al. (1999) is based on a set of marine samples whereas our samples include soil, freshwater and brackish samples. We, therefore, carried out a factor analysis on our set of samples using the program SPSS 15.0. Prior to performing the factor analysis on mol% of amino acids and other variables they were standardised by subtracting the mean of all values from individual results and dividing by the standard deviation of all measurements.

2.4.3. Stable isotopes

$\delta^{15}N$ and $\delta^{13}C$ values were determined using a Finnigan MAT 252 mass spectrometer after high-temperature flash combustion in a Carlo Erba NA-2500 elemental analyzer at 1100 °C. Pure tank N_2 calibrated against the reference standards International Atomic Energy Agency IAEA-N-1 and IAEA-N-2 was used as a working standard. $\delta^{15}N$ is given as the per mil deviation from the N-isotope

composition of atmospheric N_2. Analytical precision was better than 0.1‰ based on replicate measurements of a reference standard. Duplicate measurements of samples resulted in a mean deviation of 0.2‰. $\delta^{13}C$ was measured after the removal of carbonate by $2N\ H_3PO_4$ and is given as the per mil deviation from the isotopic composition of the PDB standard.

2.4.4. Sterols and fatty acids

Sterols and fatty acids were determined in the Yen 02 and Kara 01 samples. For lipid analyses the samples were extracted three times with dichloromethane/methanol (2:1, by volume). The total extract was transesterified using 3 N methanolic HCl (50 °C for 12 h), a method modified according to Christie (1990) and Conte et al. (1992), and separated into fractions by column chromatography after eluting with 5 ml hexane for the hydrocarbons, 4 ml dichloromethane for the fatty acids and 5 ml ethylacetate:hexane (20:80, by vol.) for the sterols. The sterols were silylated with 500 μl *bis*-trimethylsilyl-trifluoroacetamide (BSTFA) (60 °C for 2 h). All compounds were analyzed with a Hewlett Packard gas chromatograph (HP 6890, column 30 m × 0.25 mm; film thickness 0.25 μm; liquid phase: DB-5MS) using a temperature program as follows: 60 °C (2 min), 150 °C (rate: 15 °C/min), 320 °C (rate: 3 °C/min; 20 min isothermal). The injection volume was 1 μl using a cold injection system (temperature program: 60 °C (0.1 min), 320 °C (rate: 12 °C/s, 60 s)). Helium was used as carrier gas (1.5 ml/min).

The identification of the sterols and fatty acids was supported by GC/MS, which consisted of a gas chromatograph (HP 5890, column 30 m × 0.25 mm; film thickness 0.25 μm; liquid phase: DB-5MS) and a mass spectrometer (MSD, HP 5972, 70 eV electron—impact ionisation, Scan 50–650 m/z, 1 scan/s, ion source temperature 175 °C). GC analysis was performed with the following temperature program: 60 °C (2 min), 150 °C (rate: 15 °C/min), 320 °C (rate: 3 °C/min; 20 min isothermal). The injection volume was 1 μl (splitless). Helium was used as carrier gas (1.2 ml/min at 60 °C). The identification of the sterols and fatty acids was carried out on the basis of GC retention time and MS fragmentation pattern. For quantification 19:0 fatty acid methyl ester and cholest-5-en-3β-ol-2, 2,3,4,4,6-d_6 were added as internal standards before any extraction and analytical step.

For the interpretation of the sediment trap data we use four sterols, 24-methylcholesta-5,22-E-dien-3β-ol (brassicasterol), 4α,23,24-trimethyl-5α-cholest-22E-en-3β-ol (dinosterol), 24-ethylcholest-5-en-3β-ol (β-sitosterol) and 24-methylcholest-5-en-β-ol (campesterol), and four fatty acids, *cis*-11eicosenoic acid (20:1(n-9)), *cis*-13-eicosenoic acid (20:1(n-7)), and the two isomeres of *cis*-docosenoic acid (22:1 (n-11), 22:1(n-9)). All data are available on http://www.pangaea.de.

3. Results

3.1. Current speeds and directions

In the deep layer of saline water current speeds (daily averages to remove tidal signal) reached maxima of 35 cm/s in 2001/2002 and were slightly lower at the Kara than at the Yen location. Weekly averages used in Fig. 2d to elucidate the seasonality were between 3.5 and 30 cm/s. Currents speeds were highest in September/October 2001 and in October 2002–May 2003 and lower (<15 cm/s) in January 2001–August 2002. The currents flowed onshore (SE–SW) all through the sampling period which is typical for the deep water of the Kara Sea during most of the year (Harms et al., 2003).

3.2. Trap Yen 02 and Yen 04

3.2.1. Bulk components

Particle fluxes into the Yen 02 trap were between 20 mg m^{-2} d^{-1} in May 2001 and 12,936 mg m^{-2} d^{-1} in October 2002 (Table 1, Fig. 3a). Lithogenic matter made up between 70% and 83% of total material. Biogenic opal contributed between 10% and 18% with little seasonal variation. From January to June 2001 biogenic opal could not be determined as samples were on glass fibre filters (see 2.2.) so that we may have missed a small seasonal signal. Organic carbon percentages were between 2.5% and 17.6% which is a very wide range compared to other trap experiments in arctic regions (Hargrave et al., 2002; Ingalls et al., 2006; Wassmann et al., 2004). Low values (<8%) occurred from February to April, from the end of June to September 2001, and during the whole deployment period of Yen 04. Peaks occurred in May/June 2001, in October 2000 to January 2001, and in May/June 2001. Smaller peaks were observed in mid-July and in the beginning of August 2001. C/N ratios were between 7.6 and 11.7 with higher ratios in June through August 2001 (Table 1).

Table 1
Total and bulk component fluxes in $mg\,m^{-2}\,d^{-1}$, percentages of bulk components, POC/N ratios, $\delta^{15}N$, $\delta^{13}C$, amino acid and hexosamine carbon as percentage of total carbon (AAC + HAC as % of POC), degradation and reactivity index derived from amino acid spectra (DI, RI), in sediment traps Yen 02 and Yen 04. Fluxes of brassicasterol, campesterol, β-sitosterol, dinosterol and copepod fatty acids in $\mu g\,m^{-2}\,d^{-1}$ in sediment trap Yen 02

No.	Sampling interval Start	End	Total flux $mg\,m^{-2}\,d^{-1}$	Biogenic opal $mg\,m^{-2}\,d^{-1}$	Lithogenics $mg\,m^{-2}\,d^{-1}$	POC $mg\,m^{-2}\,d^{-1}$	Total N $mg\,m^{-2}\,d^{-1}$	Biogenic opal %	Lithogenics %	POC %	N %
Yenisei 02											
1	9/16/2000	9/23/2000	2898.7	266.7	2365.6	148.0	17.9	9.2	81.6	5.1	0.62
2	9/23/2000	9/30/2000	2840.8	298.6	2280.0	145.7	18.1	10.5	80.3	5.1	0.64
3	9/30/2000	10/14/2000	1002.6	123.9	731.2	81.9	10.2	12.4	72.9	8.2	1.02
4	10/14/2000	10/28/2000	909.8	101.2	643.4	91.8	12.7	11.1	70.7	10.1	1.39
5	10/28/2000	11/11/2000	478.0	49.1	347.7	45.1	5.9	10.3	72.7	9.4	1.23
6	11/11/2000	12/9/2000	448.2	45.5	320.5	45.7	5.0	10.1	71.5	10.2	1.13
7	12/9/2000	1/6/2001	500.4	44.5	373.0	46.1	5.8	8.9	74.5	9.2	1.16
8	1/6/2001	2/3/2001	147.4	nd	125.7	12.1	1.5	nd	nd	8.2	1.00
9	2/3/2001	3/3/2001	241.3	nd	227.0	7.9	1.0	nd	nd	3.3	0.42
10	3/3/2001	3/31/2001	117.0	nd	110.1	3.8	0.4	nd	nd	3.3	0.37
11	3/31/2001	4/28/2001	69.9	nd	62.9	3.9	0.4	nd	nd	5.6	0.64
12	4/28/2001	5/12/2001	21.6	nd	15.9	3.1	0.5	nd	nd	14.5	2.22
13	5/12/2001	5/26/2001	18.9	nd	12.9	3.3	0.4	nd	nd	17.6	2.06
14	5/26/2001	6/9/2001	88.6	nd	74.9	7.6	1.1	nd	nd	8.6	1.26
15	6/9/2001	6/16/2001	93.3	nd	72.1	11.7	1.2	nd	nd	12.6	1.33
16	6/16/2001	6/23/2001	474.8	nd	430.8	24.5	2.6	nd	nd	5.2	0.56
17	6/23/2001	6/30/2001	762.5	nd	713.6	27.2	3.2	nd	nd	3.6	0.42
18	6/30/2001	7/7/2001	211.7	26.1	160.4	14.0	1.4	12.3	75.8	6.6	0.66
19	7/7/2001	7/14/2001	142.2	14.2	104.7	12.9	1.3	10.0	73.6	9.1	0.91
20	7/14/2001	7/21/2001	146.3	10.5	122.1	7.6	0.8	7.2	83.5	5.2	0.55
21	7/21/2001	7/28/2001	104.8	14.8	79.8	5.6	0.6	14.2	76.2	5.4	0.53
22	7/28/2001	8/4/2001	109.4	12.7	81.7	8.3	1.0	11.6	74.7	7.6	0.87
23	8/4/2001	8/11/2001	133.3	16.6	101.1	8.7	1.1	12.4	75.8	6.5	0.81
24	8/11/2001	8/18/2001	712.3	81.8	566.8	35.4	4.0	11.5	79.6	5.0	0.56
Yenisei 04											
1	7/10/2002	14/10/2002	12935.9	2203.0	10049.5	379.7	49.8	17.0	77.7	2.9	0.39
2	14/10/2002	21/10/2002	2251.3	379.8	1719.1	84.6	12.4	16.9	76.4	3.8	0.55
3	21/10/2002	28/10/2002	2723.0	431.9	2167.2	68.9	8.8	15.9	79.6	2.5	0.33
4	28/10/2002	04/11/2002	1816.4	307.7	1402.3	59.1	7.5	16.9	77.2	3.3	0.42
5	4/11/2002	18/11/2002	1476.1	260.7	1149.0	36.9	4.1	17.7	77.8	2.5	0.28
6	18/11/2002	02/12/2002	1026.6	173.5	762.7	50.2	7.0	16.9	74.3	4.9	0.69
7	2/12/2002	16/12/2002	816.6	113.3	626.0	43.0	6.4	13.9	76.7	5.3	0.79
8	16/12/2002	30/12/2002	1599.1	265.1	1225.3	60.4	8.5	16.6	76.6	3.8	0.53
9	30/12/2002	24/02/2003	2061.5	347.8	1579.4	74.6	10.5	16.9	76.6	3.6	0.51
10	24/2/2003	21/04/2003	4127.7	680.7	3258.4	104.8	13.0	16.5	78.9	2.5	0.32

Table 1 (continued)

No.	POC/N	δ15N ‰	δ13C ‰	AA-C+HA-C as % of POC	DI	RI	Brassicasterol µg m^{-2} d^{-1}	Campesterol µg m^{-2} d^{-1}	β-Sitosterol µg m^{-2} d^{-1}	Dinosterol µg m^{-2} d^{-1}	Copepod FA µg m^{-2} d^{-1}
Yenisei 02											
1	9.7	7.49	−26.32	26.2	1.04	5.55	561.6	nd	258.6	64.4	1087.7
2	9.4	6.91	−26.02	36.4	1.09	7.38	1185.3	916.7	583.9	128.8	1008.5
3	9.4	6.76	−25.90	26.1	1.07	4.46	590.6	333.0	213.2	26.4	827.2
4	8.5	8.19	−26.10	27.7	1.35	7.64	154.6	60.9	51.7	1.5	1630.5
5	9.0	8.05	−25.91	26.5	0.74	4.98	399.9	246.2	160.3	10.5	549.8
6	10.6	9.91	−28.69	22.6	1.24	10.35	968.0	560.3	574.6	64.6	440.1
7	9.2	9.38	−28.62	24.2	1.30	4.75	752.1	405.5	447.6	59.4	437.6
8	9.5	8.60	−26.61	27.4	1.34	32.76	238.5	167.7	162.1	12.3	1015.5
9	9.1	6.95	−25.99	40.7	0.28	4.13	nd	nd	nd	nd	trace
10	10.3	2.87	−26.03	15.6	0.27	3.81	45.0	41.1	39.1	6.9	20.8
11	10.1	7.06	−26.34	22.8	0.47	6.51	21.0	nd	19.6	2.9	32.4
12	7.6	10.28	−26.67	34.3	0.86	5.08	6.4	nd	9.0	0.0	14.1
13	10.0	12.26	−26.23	51.1	1.27	22.06	48.4	28.1	28.2	2.7	44.6
14	8.0	11.87	−25.49	45.7	1.26	28.04	115.8	nd	20.8	0.0	106.9
15	11.1	8.85	−26.77	20.3	1.00	25.49	68.2	24.9	30.9	6.4	53.1
16	10.8	5.17	−27.15	15.0	0.85	12.11	308.9	nd	177.8	15.6	70.9
17	9.9	4.51	−26.48	16.9	0.29	4.55	290.5	nd	163.8	32.3	103.2
18	11.6	7.58	−27.32	6.0	0.94	5.33	229.6	59.0	81.5	12.4	68.8
19	11.7	7.73	−27.75	19.2	1.05	3.88	150.7	60.5	92.7	12.8	67.0
20	11.0	6.55	−28.52	26.7	0.63	1.78	100.4	nd	50.2	0.0	21.9
21	11.7	7.58	−27.25	31.5	0.48	2.40	86.8	36.0	55.7	9.6	20.9
22	10.2	9.20	−28.72	36.1	1.08	7.13	122.9	63.2	108.2	20.7	21.1
23	9.4	9.71	−28.56	42.5	1.28	14.32	128.1	75.5	121.4	23.8	53.6
24	10.4	5.74	−26.35	19.3	0.41	5.22	113.8	nd	80.3	27.0	77.5
Yenisei 04											
1	8.9	8.17	−24.02	22.2	−0.19	4.66	nd	nd	nd	nd	nd
2	8.0	7.75	−25.74	26.3	0.32	6.96	nd	nd	nd	nd	nd
3	9.1	6.20	−26.13	18.4	−0.05	3.03	nd	nd	nd	nd	nd
4	9.2	6.75	−26.61	21.3	0.15	4.53	nd	nd	nd	nd	nd
5	10.6	5.77	−26.31	15.5	−0.48	2.23	nd	nd	nd	nd	nd
6	8.3	9.07	−26.47	27.0	0.64	11.92	nd	nd	nd	nd	nd
7	7.8	8.49	−26.21	31.1	0.71	17.71	nd	nd	nd	nd	nd
8	8.3	9.33	−26.25	25.3	0.14	7.19	nd	nd	nd	nd	nd
9	8.3	9.10	−25.86	27.8	0.39	5.82	nd	nd	nd	nd	nd
10	9.4	7.71	−26.04	23.8	0.53	5.02	nd	nd	nd	nd	nd

nd: not determined.
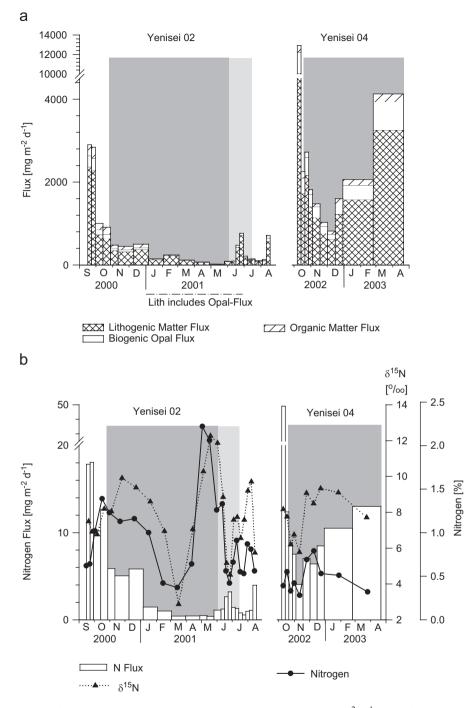Copepod fatty acids are 20:1(n−9) + 20:1(n−7) + 22:1(n−11) + 22:1(n−9).

Fig. 3. (a) Bulk component fluxes (lithogenic matter, biogenic opal, organic matter) in mg m^{-2} d^{-1} sampled by the Yen 02 and 04 traps. In indicated samples (January–June 2001) biogenic opal has not been determined so that hatched areas indicate lithogenic matter and biogenic opal. Dark shaded areas indicate complete ice cover and light shade indicates ice break up. (b) Nitrogen fluxes in mg m^{-2} d^{-1}, nitrogen percentages, and δ^{15}N values in the Yen 02 and 04 trap samples. Dark shaded areas indicate complete ice cover and light shade indicates ice break up. (c) Organic carbon fluxes in mg m^{-2} d^{-1}, organic carbon percentages and δ^{13}C values in Yen 02 and 04 samples (upper graph). Amino acid (AA) and hexosamine (HA) fluxes in mg m^{-2} d^{-1}, F 1 scores of factor analysis of trap samples, and Asp/ß-Ala ratios in Yen 02 and 04 samples (lower graph). Dark shaded areas indicate complete ice cover and light shade indicates ice break up.

Fig. 3. (*Continued*)

3.2.2. Stable isotopes, AA, hexosamines, sterols and fatty acids

The $\delta^{15}N$ values revealed a very wide range from 2.9‰ to a maximum of 12.3‰ (Fig. 3b) and were positively correlated with organic carbon and total nitrogen percentages ($R^2 = 0.41$ and $R^2 = 0.46$, respectively, $n = 34$). The correlation of AA content

and $\delta^{15}N$ was even better ($R^2 = 0.50$) implying that common processes enhanced both $\delta^{15}N$ values and (nitrogenous) organic matter contents. The correlations became more significant if the last four samples of Yen 04 were excluded.

$\delta^{13}C$ variations differed from those of $\delta^{15}N$, and organic contents during most of the year (Fig. 3b

Table 2
Annual averages of total and bulk component fluxes, weighed means of POC/N ratios, $\delta^{15}N$, $\delta^{13}C$ and annual averages of percentages of bulk components, DI and RI in sediment trap samples from Yen 02, Yen 04 and Kara Sea 01

	Yenisei 02 09/00–08/01	Yenisei 04 10/02–04/03	BP 00–14 Surface Sed.	BP 99–04 Surface Sed.	BP 00–07 Surface Sed.	Kara Sea 01 09/01–08/02	BP 00–26 Surface Sed.	BP 01–61 Surface Sed.
Latitude N	74°00, 28	74°00, 1145	72°55, 86	73°24, 9	74°39, 48	76°12, 08	75°42, 54	76°12, 9
Longitude E	80°00, 45	80°19, 6413	79°47, 4	79°40, 5	81,08, 46	75°45, 3	77°57, 6	75°53, 15
Water depth m	31	40	19.2	32.3	38	73	68	106
Trap depth m	20	29				54		
Total flux $g\,m^{-2}\,a^{-1}$	150.3	547.1[a]	650	500	350	222.3	170	70
Lithogenic flux $g\,m^{-2}\,a^{-1}$	118.7	425.9[a]	553.2	441.0	301.7	192.0	148.8	nd
Opal flux $g\,m^{-2}\,a^{-1}$	12.6	91.1[a]	66.3	42.5	34.3	15.6	15.5	nd
POC flux $g\,m^{-2}\,a^{-1}$	10.6	16.7[a]	13.0	7.8	2.6	8.2	2.7	0.7
N flux $g\,m^{-2}\,a^{-1}$	1.30	2.21[a]	1.40	0.95	0.35	1.17	0.36	0.12
C/N (atomic)	9.5	8.8	11.1	9.5	8.8	8.2	8.8	6.9
$\delta^{15}N$ ‰	7.99	8.21	5.28	5.70	6.99	7.47	7.05	6.98
$\delta^{13}C$ ‰	−26.88	−25.77	−26.96	−26.37	−26.15	−24.12	−24.92	−24.39
Lithogenic matter %	79.0	77.9	85.0	88.2	86.2	86.4	87.5	nd
Biogenic opal %	8.4	16.7	11.0	8.5	9.8	7.0	9.1	nd
POC %	7.1	3.1	2.0	1.6	0.8	3.7	1.6	1.0
N %	0.87	0.40	0.21	0.19	0.10	0.52	0.21	0.17
DI	0.90	0.22	nd	−0.53	−0.81	−0.05	−1.19	nd
RI	9.57	6.91	nd	1.51	1.01	5.43	0.21	nd

For Yen 02 and Kara Sea 01 fluxes have been extrapolated to one year based on average fluxes of 11 months. For trap Yen 04 fluxes have been averaged for the 195.5 days of deployment.
Accumulation rates in surface sediments (0–2 ka) taken from Table 7.6.2. in Stein and Fahl (2004) and accumulation rates of lithogenic matter, biogenic opal, organic carbon (POC) and nitrogen (N) calculated rom our bulk component measurements and total accumulation rates. POC/N ratios, $\delta^{15}N$, $\delta^{13}C$, percentages of bulk components, DI and RI in surface sediments.
[a] $g\,m^{-2}\,195.5\,d^{-1}$.

and c). Minima occurred in November/December 2000 and June to August 2001. The weighted annual averages in Yen 02 (Yen 04) were 8.0‰ (8.2‰) and −26.9‰ (−25.8‰) for $\delta^{15}N$ and $\delta^{13}C$, respectively (Table 2). AA carbon contributed 15–40% to total organic carbon and AA nitrogen contributed 40–95% to total nitrogen and had maximum values in May/June and August 2001.

All sterol fluxes (brassicasterol, dinosterol, β-sitosterol and campesterol) showed similar seasonal patterns that are correlated to those of other organic components (Table 1). Flux maxima occurred in September and in the beginning of October 2001 as well as during November/December 2000 when the maximum concentrations were attained. A third but lower maximum was found in June/August 2001. The fluxes of brassicasterol and campesterol showed values from 10 to more than $1000\,\mu g\,m^{-2}\,d^{-1}$, whereas the fluxes of β-sitosterol and dinosterol were lower with maxima of 500 and $130\,\mu g\,m^{-2}\,d^{-1}$, respectively (Table 1). The highest fluxes of the 20:1 and 22:1 fatty acids (both isomers) occurred from October 2000 to January 2001, reaching rates of $1600\,\mu g\,m^{-2}\,d^{-1}$. During the other

months of the year these values were distinctly lower (1/10–1/100).

3.4. Trap Kara 01

3.4.1. Bulk components

Particle fluxes at the Kara 01 location were between $80\,mg\,m^{-2}\,d^{-1}$ in September 2001 and $1320\,mg\,m^{-2}\,d^{-1}$ in July/August 2002. Maxima occurred in January/February and August and minima in the first cup (September) and in April to mid-June (Table 3; Fig. 4a). Except for the first cup that had exceptionally high organic carbon contents of almost 22%, the composition of the material was very similar in all cups. Lithogenic matter contents were between 81% and 90%, biogenic opal contents were 6–8% and organic carbon contents 2.4–6.5% (Table 3). Maxima of organic carbon contents occurred in September/ October 2001 and in June–August 2002 and were accompanied by minima of lithogenic matter contents. C/N ratios were between 6.7 and 9.7.

Table 3

Total and bulk component fluxes in $mg\,m^{-2}\,d^{-1}$, percentages of bulk components, POC/N ratios, $\delta^{15}N$, $\delta^{13}C$, amino acid and hexosamine carbon as percentage of total carbon (AAC+HAC as % of POC), degradation and reactivity index derived from amino acid spectra (DI, RI), fluxes of brassicasterol, campesterol, and β-sitosterol in $\mu g\,m^{-2}\,d^{-1}$ in sediment trap Kara Sea 01

No.	Sampling interval Start	Sampling interval End	Total flux $mg\,m^{-2}\,d^{-1}$	Biogenic opal $mg\,m^{-2}\,d^{-1}$	Lithogenics $mg\,m^{-2}\,d^{-1}$	POC $mg\,m^{-2}\,d^{-1}$	Total N $mg\,m^{-2}\,d^{-1}$	Biogenic opal %	Lithogenics %	POC %	N %
1	4/9/2001	21/9/2001	79.6	5.7	42.7	17.4	2.5	7.2	53.6	21.8	3.20
2	21/9/2001	2/11/2001	437.7	34.7	359.2	24.3	4.2	7.9	82.1	5.6	0.97
3	2/11/2001	28/12/2001	904.9	72.7	793.2	21.7	3.2	8.0	87.7	2.4	0.36
4	28/12/2001	22/2/2002	1228.7	73.1	1100.3	30.7	4.2	6.0	89.6	2.5	0.35
5	22/2/2002	19/4/2002	282.2	19.5	242.0	11.5	1.9	6.9	85.8	4.1	0.67
6	19/4/2002	31/5/2002	144.9	10.4	127.0	4.2	0.7	7.2	87.7	2.9	0.48
7	31/5/2002	14/6/2002	116.2	8.3	94.1	7.6	1.1	7.2	81.0	6.6	0.94
8	14/6/2002	28/6/2002	189.6	13.6	155.8	11.2	1.6	7.2	82.2	5.9	0.84
9	28/6/2002	26/7/2002	807.4	54.0	676.2	42.9	5.1	6.7	83.8	5.3	0.63
10	26/7/2002	9/8/2002	1320.9	99.6	1082.5	77.1	9.2	7.5	81.9	5.8	0.70

No.	POC/N	$\delta^{15}N$ ‰	$\delta^{13}C$ ‰	AA-C+HA-C as% of POC	DI	RI	Brassicasterol $\mu g\,m^{-2}\,d^{-1}$	Campesterol $\mu g\,m^{-2}\,d^{-1}$	β-Sitosterol $\mu g\,m^{-2}\,d^{-1}$
1	7.9	8.54	−25.36	nd	nd	nd	224.8	382.0	202.5
2	6.7	8.08	−23.90	30.1	0.38	7.71	432.5	342.5	285.6
3	7.9	7.26	−24.13	19.8	−0.51	1.64	233.7	154.3	183.2
4	8.5	6.77	−24.75	17.5	−0.24	2.23	315.6	199.5	277.2
5	7.1	9.11	−24.11	27.8	0.16	8.84	42.6	22.9	67.8
6	7.0	10.52	−23.76	27.4	0.03	4.35	41.9	33.2	40.9
7	8.1	9.08	−22.21	12.1	−0.24	2.58	66.9	65.9	45.9
8	8.2	6.11	−22.21	10.7	−0.33	4.85	51.9	36.2	57.8
9	9.8	6.92	−23.24	19.1	0.29	9.54	342.6	160.0	300.6
10	9.7	6.61	−24.45	17.9	0.02	7.18	1214.8	203.8	419.6

nd: not determined.

3.4.2. Stable isotopes, AA, hexosamines, sterols and fatty acids

The $\delta^{15}N$ values of the Kara 01 samples were between 6.6‰ and 10.5‰; highest values occurred in the low flux period from March to the beginning of June (Fig. 4b). $\delta^{13}C$ values were between −22.2‰ and −25.4‰ and had their maximum in May/June (Fig. 4c). Weighted mean values of the whole deployment were 7.5‰ and −24.1‰ for $\delta^{15}N$ and $\delta^{13}C$, respectively (Table 2). AA and
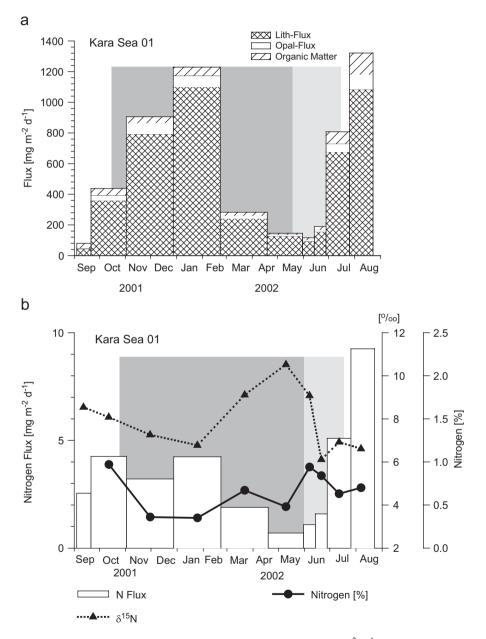

Fig. 4. (a) Bulk component fluxes (lithogenic matter, biogenic opal, organic matter) in mg m^{-2} d^{-1} sampled by the Kara Sea 01 trap. Dark shaded area indicates complete ice cover and light shade indicates ice break up. (b) Nitrogen fluxes in mg m^{-2} d^{-1}, nitrogen percentages, and $\delta^{15}N$ values in the Kara Sea 01 trap samples. Dark shaded area indicates complete ice cover and light shade indicates ice break up. (c) Organic carbon fluxes in mg m^{-2} d^{-1}, organic carbon percentages and $\delta^{13}C$ values in Kara Sea 01 samples (upper graph). Amino acid and hexosamine fluxes in mg m^{-2} d^{-1}, F 1 scores of factor analysis of trap samples, and Asp/ß-Ala ratios in Kara Sea 01 samples (lower graph). Dark shaded area indicates complete ice cover and light shade indicates ice break up.
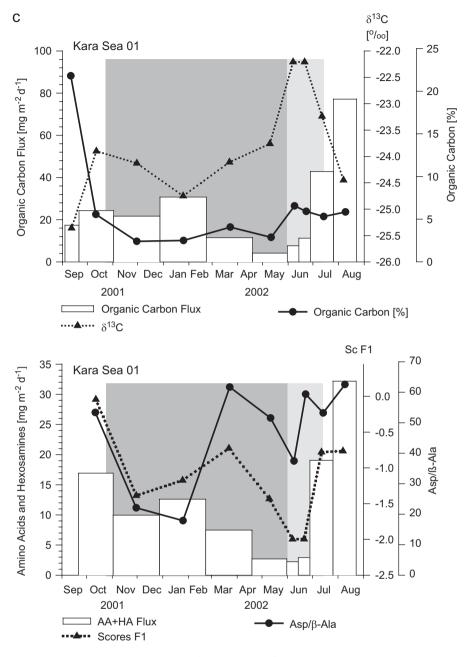
Fig. 4. (*Continued*)

hexosamines contributed 11–30% to total organic carbon and 23–55% to total nitrogen. Minima corresponded with the high $\delta^{13}C$ values in June. Unlike the Yenisei samples there were no significant correlations among the measured variables.

Campesterol and β-sitosterol had nearly the same flux pattern throughout the year with high fluxes of up to $400\,\mu g\,m^{-2}\,d^{-1}$ except from March to June (Table 3). The brassicasterol fluxes reached values

around $300\,\mu g\,m^{-2}\,d^{-1}$ from September 2001 to February 2002 and a flux maximum of $1200\,\mu g\,m^{-2}\,d^{-1}$ in September 2002 (Table 3). The bassicasterol pattern nearly paralleled the record of organic carbon flux. No dinosterol could be detected and the fatty acid (20:1 and 22:1) contents were rather low, reaching not more than trace amounts in some months and are, therefore, not given.

4. Discussion

4.1. Relation of fluxes to ice cover, light availability and river discharge

Particle fluxes at both trap locations had maxima during the ice free as well as the ice covered seasons (Fig. 2c) which is in contrast to other studies from seasonally ice covered regions (Hargrave et al., 2002; Honjo et al., 2000; Ingalls et al., 2006; Ramseier et al., 1997; Wassmann et al., 2004). The high river discharge by the Yenisei in June and the Ob in June to August (Fig. 2a) was reflected in only slightly enhanced fluxes during these months (Fig. 2c). This could imply that much of the riverine particulate matter was kept in suspension during the summer months and settled later in the year (4.3.2.). Sufficient light to initiate a plankton bloom ($>15\,\mathrm{W\,m^{-2}}$; Gowen et al., 1995) was available from March to September. The ice cover as well as the high concentration of suspended matter from the rivers, however, probably prevented an intense bloom with enhanced particle fluxes in early spring and summer (see 4.3.2.).

The pattern of current speeds (Fig. 2d) did not correspond with the particle flux pattern (Fig. 2c). This would be the case if we had a strong sampling artefact due to overtrapping in periods of high current speeds (Gust et al., 1992; Gust and Kozerski, 2000). We can thus exclude that the flux was significantly modulated by current related changes in sampling efficiency.

4.2.1. Sources and degradation of organic matter in the Kara Sea: Stable isotopes

δ^{13}C values were used in previous studies to quantify terrestrial input into the Kara Sea (Fernandes and Sicre, 1999; Krishnamurthy et al., 2001) as well as into other Arctic shelf seas (Goni et al., 2005; Guo et al., 2004a, 2004b). Highest δ^{13}C values measured in our study were about -22‰ (Tables 1 and 3). This was lighter than the marine end member in lower latitudes due to the better CO_2 dissolution in colder water (Sackett et al., 1974). River sediments had minima of δ^{13}C around -29‰ in the Ob and -27‰ in the Yenisei (Fahl et al., 2003; Nagel et al., submitted) which was close to Kara Sea terrestrial end member δ^{13}C values of -27.8‰ and -27‰ used by Fernandes and Sicre (1999) and Krishnamurthy et al. (2001), respectively. The δ^{13}C of trap samples showed a wide range. Average δ^{13}C values at the Yen locations were closer to the terrestrial end member whereas the average δ^{13}C of Kara 01 samples was closer to marine and estuarine phytoplankton (Table 2; Fig. 5).
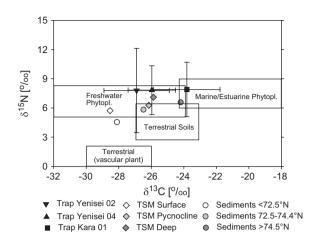

Fig. 5. Mean values and standard deviations of δ^{13}C vs. δ^{15}N in sediment trap samples from the Yen 02, 04 and Kara Sea 01 stations. Ranges for freshwater phytoplankton, marine/estuarine plankton, terrestrial soils and vascular plant (after McCallister et al., 2004) are indicated. Also indicated are mean values in TSM and sediments from the Kara Sea (after Nagel et al., submitted).

Terrigenous organic matter in the Kara Sea can also be identified by low δ^{15}N values. The terrestrial end member δ^{15}N values are around 4.5‰ in the Ob and less than 3‰ in the Yenisei, respectively (Nagel et al., submitted). Investigations of Guo et al. (2004a) showed that the δ^{15}N in Siberian river sediments decrease from west to east. This is probably related to the eastward increase in permafrost area and thickness (Stolbovoi and McCallum, 2002) which could lead to a better preservation of soil organic matter. As will be shown below (4.3.) the periods of maximum river discharges to the Kara Sea could be discerned from both, low δ^{13}C and δ^{15}N values in trap material.

Surface sediments showed a characteristic increase of δ^{13}C and δ^{15}N towards the north, similar to average trap values, reflecting a change from terrestrial to marine dominance (Fig. 5). The northern Kara Sea sediments had δ^{15}N values of more than 7‰ which is about 2‰ higher than average marine nitrate (Sigman et al., 2000) but similar to other sediments from the Arctic Ocean (Schubert and Calvert, 2001). Suspended matter had a more terrestrial signal in surface waters and a marine imprint at depth which could be due to the onshore flow of deep water as well as the resuspension of sediments (Nagel et al., submitted).

Most δ^{15}N of trap samples were higher than those of phytoplankton end members, suspended matter and surface sediments. There are several possible explanations for these higher values. δ^{15}N may

reflect not only organic matter sources but also transformation processes within the nitrogen cycle (Altabet, 1996). Isotopic fractionation during nitrogen uptake results in an increase of the $\delta^{15}N$ of the substrate as well as the produced organic matter as nutrients become depleted during a progressing plankton bloom (Altabet, 1996). This process may explain the high $\delta^{15}N$ values of Yenisei samples from an early plankton bloom in the polynya area (see 4.3.). High $\delta^{15}N$ values can also indicate the contribution from zooplankton as well as their fecal pellets as each increase in trophic level is accompanied by a $\delta^{15}N$ increase by about 3–4‰ (Montoya et al., 1991). This may be responsible for high $\delta^{15}N$ values of autumn and winter samples from the Yenisei location (see 4.3.). Finally, $\delta^{15}N$ values can increase during diagenesis of sinking particles and sediments due to organic matter degradation (Altabet et al., 1999; Lourey et al., 2003; Smith et al., 2002). However, a strong isotopic imprint is probably restricted to degradation processes in the deep sea; near shore and slope sediments showed no significant $\delta^{15}N$ increase in sediments compared to sinking particles which was probably related to faster burial and oxygen depletion in the sediments (Altabet et al., 1999; Gaye-Haake et al., 2005). Kara Sea trap samples with higher $\delta^{15}N$ values were, generally, less degraded (see 3.2. and 4.3.) so that differences in nitrogen sources and increasing trophic levels may be responsible for higher $\delta^{15}N$ values in the Kara Sea rather than organic matter degradation.

4.2.2. Sources and degradation of organic matter in the Kara Sea: AA

AA are among the more labile organic constituents and serve as a major food source to heterotrophs. In order to study the factors responsible for changes in AA composition we carried out a factor analysis on 18 normalized mol% values of amino acids measured in a set of 213 samples from the Kara Sea. These consist of three samples from the fresh water end member, three soil and root samples, 102 suspended matter samples from the estuaries to the open marine environment, 62 surface sediment samples and 43 sediment trap samples (see Tables 1 and 3). Similar to the results of other studies (Dauwe and Middelburg, 1998; Ingalls et al., 2003) the AA enriched in fresh plankton have highest component scores for factor 1 (F1) whereas the amino acids enriched during organic matter degradation have higher component scores for factor 2 (F2). Generally, the component

loadings for F1 are similar to those of Dauwe et al. (1999) used for the calculation of the DI. In order to classify the Kara Sea trap samples according to their state of degradation we plotted the RI (see 2.4.4.) of Kara Sea samples against their site scores for F1 (Fig. 6) which is very similar to the RI-DI plot of Unger et al. (2005). It elucidates the large variations of degradation states of trap samples ranging from values typical of fresh surface suspension to those of surface sediments. Organic matter of the Yen 02 trap is, mostly, in the range of surface suspension whereas Yen 04 and Kara 01 samples are more similar to deep suspension; the low RI and F1 site scores of some of their samples may even indicate contribution from resuspended sediments. River suspension of the Yenisei sampled in September is in the range of brackish and marine surface suspension whereas samples taken during the peak discharge period in June from Salekhard on the Ob are more degraded (Fig. 6). This could be due to the addition of soil organic matter to the Ob suspension which degradation state is close to that of deep suspended matter (Fig. 6).

Dauwe et al. (1999) pointed out that the changes in the monomer distribution determining the DI are not always linear with increasing degradation. This is confirmed by our study that shows that the major changes in the RI occur in relatively fresh organic matter having high RI and F1 scores, whereas the major differences in F1 scores occur between the more degraded trap samples and sediments. The F1 site score-RI plot, thus, helps to classify samples of
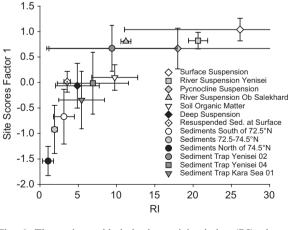

Fig. 6. The amino acid derived reactivity index (RI) plotted against the F1 scores of a factor analyzes of mol% amino acids of a set of 213 samples from the Kara Sea. Mean values and standard deviations are given for suspended matter of different depths, river end members, soils samples, sediments from different latitudes and the three trap deployments.

variable environments according to their state of degradation.

4.3. Seasonal variations

4.3.1. Factor analyses of trap samples

A second factor analysis was carried out on the trap samples only, using the mol% of 18 AA, organic carbon, nitrogen, and AA + hexosamine contents, the DI, RI, $\delta^{15}N$ and $\delta^{13}C$. The AA enriched in fresh organic matter (Arg, Val, Lys, Ile, Leu, Phe, His, Tyr), organic carbon, nitrogen and AA + hexosamine contents as well the indicators of organic matter freshness DI and RI have high component scores for F 1 (Fig. 7a). Moreover, $\delta^{15}N$ is associated with this group of variables indicating that organic matter of a less degraded source in Kara Sea trap samples is characterised by higher $\delta^{15}N$ values.

The second group of variables has lower F1 and higher F2 scores and includes the AA enriched by degradation such as ß-Ala, γ-Aba, Orn and Gly (Fig. 7a) as well as Ala, Met, Ser and Thr. Of these Ser and Thr are, generally assumed to be enriched in diatoms together with Gly (Hecky et al., 1973; Ingalls et al., 2006). Ser, Thr and Gly may, therefore be considered as a separate third group of amino acids associated with biogenic opal (Ingalls et al., 2006).

A fourth group has low F1 and F2 scores and includes Asp and Glu as well as $\delta^{13}C$. Very similar results were obtained by Ingalls et al. (2006) in their PCA carried out on trap samples from the Southern Ocean using AA and pigments. They attributed the separation of Asp and Glu to the association of these AA with carbonaceous organisms. However, the Kara Sea samples had calcium carbonate contents below the detection limit of carbonate measurements so that we can exclude this source. The association of the acidic AA with $\delta^{13}C$ implies that they indicate marine vs. terrestrial material. The AA spectra from the Kara Sea trap samples thus reflect, both, organic matter degradation as well as organic matter sources.

The factor scores for F1 and F2 for trap samples show that samples from the Yenisei location mainly differ in their state of degradation (Fig. 7b). Less degraded material characterised by high F1 and low F2 scores is mostly from the autumn and early spring samples of the Yenisei 02 deployment while the most degraded samples with low F1 and high F2 scores are those with the highest contribution of
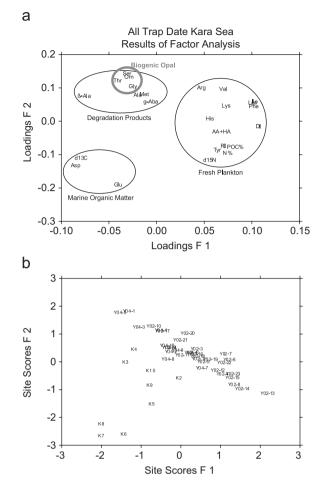
Fig. 7. (a) Variable loadings for factor 1 (F1) and factor 2 (F2) of a factor analysis of mol% amino acids, $\delta^{13}C$ (d13C), $\delta^{15}N$ (d15N), nitrogen% (N %), organic carbon % (POC %), amino acid and hexosamine in mg/g (AA + HA), the RI and the DI. The compounds are divided into four groups: "fresh plankton", "degradation products", "biogenic opal" and indicators of "marine organic matter". Gly is part of the "biogenic opal" and "degradation products" group; Met and Ala cannot be considered as degradation indicators but for unknown reasons plot within the latter group. (b) Site scores of F1 and F2 of individual trap samples from the Yenisei 02 (Y02), Yenisei 04 (Y04) and Kara Sea (K) deployments.

resuspended sediments from the ice covered season of the Yen 04 deployment. In contrast to the Yen samples the Kara samples have lower F1 and F2 scores revealing the more marine organic matter source rather than the state of degradation.

4.3.2. Seasonality of fluxes at Yen 02 and 04

4.3.2.1. Ice-free period in autumn.
Highest particle fluxes of both trap deployments occurred in September/October just before ice formation started

(Figs. 3a and 8) and were in the same order of magnitude as late summer/early autumn fluxes in other arctic coastal seas (Wassmann et al., 2004). Intermediate organic carbon and nitrogen percentages and organic matter quality indicate mixed planktonic and fluvial organic matter source (Figs. 3b, c and 8). This is confirmed by intermediate $\delta^{15}N$ values and microscopic investigations of Nöthig (2005, personal communication). Ice-free conditions and better light availability due to less river input allowed increased primary productivity in autumn and at the same time promoted enhanced settling of river material which was partly still in suspension in autumn. Short-term trap deployments and suspended matter sampling identified an intense plankton bloom off the Ob estuary in September 1999 (Nöthig et al., 2003; Gaye-Haake et al., 2003). However, in the subsequent years no such blooms were found (Unger et al., 2005). This shows that hydrographic conditions during the ice-free season were spatially and temporally very variable related to atmospheric forcing, i.e. changing wind conditions and pulsed

river input so that productivity was patchy and changed rapidly.

4.3.2.2. Ice covered season. In mid- to the end of October as the Kara Sea became fully ice covered particle fluxes were still relatively high (Fig. 8). The river suspension which had been transported to the region during the discharge peaks earlier in the year, evidently, settled during this season. A study in the Laptev Sea showed that the fluvial material remained in suspension during the season of maximum river discharge, probably due to high current speeds and turbulence, and settled later in the year at reduced energy levels (Wegner et al., 2003).

From October 2000 through January 2001 and in November/December 2002 organic matter contents and $\delta^{15}N$ values increased and high F1 scores and Asp/ß–Ala ratios indicate that organic matter was fresh (Figs. 3 and 8). During this season in 2000 (Yen 02) a large number of zooplankters and their larvae entered the cups (Nöthig, unpublished). They provided the fresh tissue enriched in ^{15}N (Montoya et al., 2002). Although zooplankters were picked
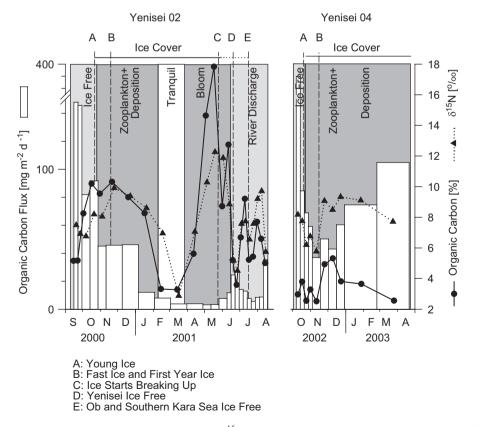

Fig. 8. Organic carbon fluxes, organic carbon percentages and $\delta^{15}N$ values in Yen 02 trap samples. Indicated are different phases of sedimentation as well as ice conditions as described in the text.

from the cups, their partial disintegration, evidently, left an imprint on the trap samples. This was also indicated by the high fluxes of 20:1 and 22:1 fatty acid isomers (Table 1) which are synthesized mainly by copepods (Falk-Petersen et al., 1987). In a study from the Fram Strait (Werner, 2006) found that many copepods reproduced under the ice in winter and may have fed on POC which is abundant during this season. The δ^{13}C minimum in November/December 2000 (Fig. 3c) either indicated an event of lateral supply and redeposition of terrestrial material from the inner estuary or resulted from a zooplankton species strongly depleted in ^{13}C (Smith et al., 2002). Sterols support the terrestrial source: they had high fluxes as well as their maximum contents (not shown) in these two cups (Table 1). Whereas campesterol and ß-sitosterol are derived from higher land plants (Huang and Meinschein, 1976; Volkmann, 1984), dinosterol and brassicasterol can be derived from both fresh water and marine algae (Fahl and Stein, 1999; Robinson et al., 1984; Thiel, 1993; Yunker et al., 1995). As fluxes and contents of all sterols were significantly correlated we can assume that the algal sterols were mainly fresh-water derived. This terrestrial signal was, however, not reflected in δ^{15}N values, possibly due to the lower nitrogen content of sediments.

During the ice covered season in 2003 (Yen 04) the proportion of lithogenic matter as well as δ^{13}C values were higher than during the Yen 02 deployment. This more marine signal could be explained by a higher proportion of resuspended material from further off shore in 2003 while material settling in 2001 was derived from more in shore source areas.

In February to April 2001 (Yen 02) the fluxes were very low and all variables attained their minima (Figs. 3a–c and 8). The low δ^{15}N values indicate riverine origin of organic matter. The small amounts of material caught in the trap during this period were thus; either slow settling degraded river suspension or reworked riverine sediment. Such a tranquil period was not observed during the Yen 04 deployment indicating that sedimentation in the Kara Sea is highly dynamic and subjected to interannual variations not only during ice-free conditions but also under ice cover. Some of the differences between the two deployments may, moreover, be due to the slight shift of the position.

4.3.2.3. Ice break up and fluvial supply. In April/May 2001 just prior to and during the first break up

of the ice cover and polynya formation trap material had peak organic carbon and nitrogen contents and organic matter was freshest of all Yen trap samples (Fig. 3a–c). The latter was discerned from maxima of F1 scores, RI, Asp/ß–Ala ratios as well as highest contributions of AA carbon to total organic carbon (Table 1; Fig. 3c). These signals were due to an ice-associated bloom that was dominated by diatoms (Nöthig, 2006, personal communication). Although fluxes remained low during this period (Fig. 8) the early bloom may have been very important to sustain the life cycles of other organisms such as protozoa, zooplankton or fish. It produced a marine, i.e. an enriched δ^{13}C signal and was, moreover, characterised by the maximum of δ^{15}N values. This may have been due to the regime in which ice-associated blooms occurred: due to low light availability the diatoms could only survive just below the ice or in the polynyas opening up in the southern Kara Sea. The ice melting produced fresh water lenses leading to stratification of surface waters so that nitrogen became limiting and was completely taken up which is evident from δ^{15}N values up to $>12‰$.

In June/July the Kara Sea was still ice covered except for the polynya area. The river plumes broke up the ice in the rivers and estuaries within less than one week in mid-June 2001 for the Yenisei and in mid-July for the Ob. The whole Kara Sea was ice free only in the beginning of August (http://www.seaice.de). The arrival of the river plumes as well as the timing of ice break up in the Kara Sea reveal slight interannual variations. Although fluxes of this phase were low, composition of material clearly reflected the fluvial input in their depleted δ^{15}N and δ^{13}C signals as well as low organic carbon and nitrogen contents and intermediate organic matter quality (Fig. 3b and c). δ^{15}N dropped to values close to the river end members (sea above) and δ^{13}C values dropped from more than $-26.5‰$ to the purely riverine value of $-28.5‰$. The relatively low fluxes found during this season were possibly due to high current speeds in surface waters as well as strong stratification which held much of the particulate matter in suspension until autumn or even winter, similar to processes found in the Laptev Sea (Wegner et al., 2003).

4.3.3. Seasonality of fluxes at Kara 01

Enhanced primary productivity during the very short ice-free period in summer was reflected in high

fluxes and/or high contents of organic matter in September/October 2001 and July/August 2002 (Fig. 4). Organic matter contents were higher and organic matter was fresher (higher Asp/ß–Ala ratios) indicating the higher contribution from primary production during the ice-free period. As pointed out above (see 4.3.1.), F1 scores can indicate terrestrial vs. marine organic matter sources as well as the state of organic matter degradation at the Kara location. Unlike the Yen trap results, F1 scores are not correlated with organic contents or Asp/ß–Ala ratios but have a minimum during ice break up coinciding with high $\delta^{13}C$ values. This shows the degraded marine nature of organic matter deposited during ice melt.

The flux pattern during the ice covered season resembled the pattern observed during the Yen 02 deployment one year before (Figs. 3 and 4) with high particle fluxes including land plant derived sterols from October to January and lowest fluxes in late winter/early spring (Table 3). Another similarity was the maximum of $\delta^{15}N$ in May/June that we attributed to an ice-associated bloom. The observed variations in stable isotopic ratios, organic matter contents and values of AA derived biogeochemical indicators were, however, smaller than those at the southern trap location and there were no correlations among these variables. One reason for this could be the, generally, more uniformly marine character of deposited organic matter at the Kara compared to the Yen location. This is also indicated by higher $\delta^{13}C$ values, the stronger degradation of organic matter as well as the different sterol spectra. In contrast to the Yen 02 results not all sterol fluxes are correlated in the Kara samples. The algal derived brassicasterol had high fluxes after ice break up in 2002 whereas the land plant derived campesterol and ß-sitosterol did not increase significantly (Table 3). We can, therefore, assume that the high brassicasterol flux was of marine origin (Yunker et al., 1995) and that the flux peak at the Kara 01 location occurring after ice break had only a weak land derived component.

4.4. Comparison of trap results with primary productivity and sediment accumulation rates

To study the fate of terrestrial and marine organic carbon in the Kara Sea we calculated the proportion of terrestrial organic matter in selected samples by a two-end member-mixing model

Terrestrial Organic Matter %

$$= \left[\frac{\delta^{13}Cmarine - \delta^{13}Corganic}{\delta^{13}Cmarine - \delta^{13}Cterrestrial} \right] 100,$$

where $\delta^{13}Cmarine$ is the marine end member of $-22‰$, $\delta^{13}Corganic$ is the $\delta^{13}C$ value of a surface sediment or of the average of trap samples, and $\delta^{13}Cterrestrial$ is the terrestrial end member of $-28‰$ (see 4.2.1.).

Based on these results we calculated the accumulation rates of marine and terrestrial organic carbon in surface sediment samples and in sediment traps as annual averages (Table 2). Samples were selected in a profile from the Yenisei estuary to the Kara Sea trap location (Figs. 1 and 9). The proportion of terrestrial organic carbon in traps and surface sediments is reduced from more than 80% at the southernmost station to 40% at the northernmost station close to the Kara Sea trap; the accumulation rate of terrestrial organic carbon drops from 10.7 to $0.3 \, g \, C \, m^{-2} \, a^{-1}$ (Fig. 9).

A comparison of accumulation rates of marine organic carbon in traps and sediments with primary production is difficult as data are neither available for the period of study nor in spatial resolution. We can only use an estimate of about $22 \, g \, C \, m^{-2} \, a^{-1}$ of Vinogradov et al. (2000) which is an average for the whole Kara Sea. Our comparison to this estimate shows that 9–28% of primary production was caught in the traps (Fig. 9). The large difference between the Yen 02 and 04 traps could indicate interannual or spatial variations of primary production as well as of resuspension, redeposition, and source of this material (see 4.3.). The preservation of marine organic carbon in surface sediments is reduced from 10% of primary productivity in the southern Kara Sea to 2% in the central Kara Sea. Northward decreasing organic matter quality is also indicated by lower organic carbon and nitrogen percentages as well as lower DI and RI values (Table 2). The stronger degradation in the central Kara Sea may be due to the lower total sediment accumulation rates (Table 2).

Composition of material caught in sediment traps and accumulated in surface sediments is similar except for organic carbon (Table 2). Degradation results in a reduction of organic carbon percentages from 3 to 7% in traps to 0.7–2% in sediments and a relative enhancement of lithogenic matter from 80 to 85% in traps to 86–88% in sediments. Biogenic opal contents are roughly around 10% in traps and sediments revealing that opal dissolution is not
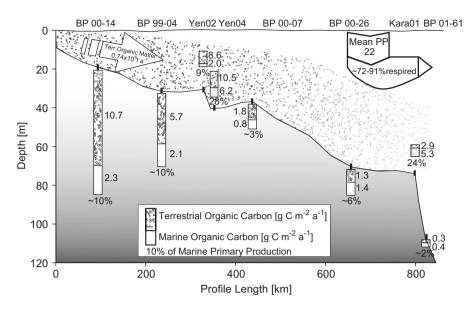
Fig. 9. Accumulation rates of marine and terrestrial organic matter in Kara Sea traps (Yen 02, Yen 04, Kara 01) and sediments (BP 00-14; BP 99-04; BP 00-07; BP 00-26; BP 01-61). All numbers are in $gC m^{-2} a^{-1}$ when not indicated differently; all percentages indicate marine organic matter as proportions of mean primary productivity. Number for mean PP is from Vinogradov et al. (2000); the amount of terrestrial organic matter is taken from Gebhardt et al. (2004); respiration in the water column has been estimated from marine organic matter accumulation in traps. Note that the bar scales are different for traps and sediments.

significant. Considering the biases of sediment trapping in a shelf environment (see 2.2.) as well as the different time scales covered by traps ($<1a$) and surface sediments (2 ka) it is remarkable that not only the composition but also the accumulation rates are roughly similar in traps and sediments.

5. Conclusions

1. In analogy to surface sediment data, particulate matter fluxes in sediment traps have a decreasing fluvial imprint from the southern to the central Kara Sea.
2. The season of ice break up in May/June is characterised by an early bloom of ice-associated algae in the polynya area of the southern Kara Sea. This bloom does not produce increased fluxes but fresh organic matter that may be important to sustain the life cycles of organisms after a period of light limitation. In the central Kara Sea settling particles caught during ice break up are of degraded marine nature and are dominated by material released during ice melt.
3. The season of main river discharge in June to August is characterised by low material fluxes in the southern Kara Sea that are of terrestrial origin.

4. Peak fluxes occur during the ice-free season in September/October and organic matter is of mixed terrestrial and planktonic origin.
5. High fluxes occur during the ice covered season in all traps and show that the riverine material supplied earlier can settle only as current speeds in surface waters decrease. Microscopic and biogeochemical evidence show that zooplankton reproduce in early winter. Moreover, resuspension, lateral transport and resedimentation determine sedimentation processes during the ice covered season.
6. Despite the possible methodological biases of sediment traps in shallow water and the different time scales of sediment trapping and surface sediment accumulation, total annual fluxes in traps are in the same order of magnitude as accumulation rates in surface sediments and have a similar composition.
7. Terrestrial organic carbon accumulation rates in sediments decrease by a factor of 30 from the southern to the central Kara Sea while the contribution of terrestrial to total organic carbon in traps and sediments decreases from $>80\%$ to 40%.
8. Marine organic carbon preservation in surface sediments is reduced from 10% of primary

production in the estuaries to 2% in the central Kara Sea which is probably related to decreasing rates of sedimentation.

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