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On the biogeochemical signature of the Lena River from its headwaters to the Arctic Ocean

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Abstract

The Lena River integrates biogeochemical signals from its vast drainage basin and its signal reaches far out over the Arctic Ocean. Transformation of riverine organic carbon into mineral carbon, and mineral carbon into the organic form in the Lena River watershed, can be considered a quasi-equilibrated processes. Increasing the Lena discharge causes opposite effects on total organic (TOC) and inorganic (TCO_2) carbon: TOC concentration increases, while TCO_2 concentration decreases. Significant interannual variability in mean values of TCO_2, TOC, and their sum (TC) has been found. This variability is determined by changes in land hydrology which cause differences in the Lena River discharge, because a negative correlation may be found between TC in September and mean discharge in August (a time shift of about one month is required for water to travel from Yakutsk to the Laptev Sea). Total carbon entering the sea with the Lena discharge is estimated to be almost 10 Tg C y^{-1}. The annual Lena River discharge of particulate organic carbon (POC) may be equal to 0.38 Tg (moderate to high estimate). If we instead accept Lisytsin's (1994) statement concerning the precipitation of 85–95% of total particulate matter (PM) (and POC) on the marginal "filter", then only about 0.03–0.04 Tg of POC reaches the Laptev Sea from the Lena River. The Lena's POC export would then be two orders of magnitude less than the annual input of eroded terrestrial carbon onto the shelf of the Laptev and East Siberian seas, which is about 4 Tg. The Lena River is characterized by relatively high concentrations of primary greenhouse gases: CO_2 and dissolved CH_4. During all seasons the river is supersaturated in CO_2 compared to the atmosphere: up to 1.5–2 fold in summer, and 4–5 fold in winter. This results in a narrow zone of significant CO_2 supersaturation in the adjacent coastal sea. Spots of dissolved CH_4 in the Lena delta channels may reach 100 nM, but the CH_4 concentration decreases to 5–20 nM towards the sea, which suggests only a minor role of riverborne export of CH_4 for the East Siberian Arctic Shelf (ESAS) CH_4 budget in coastal waters. Instead, the seabed appears to be the source that provides most of the CH_4 to the Arctic Ocean.

BGD

8, 2093–2143, 2011

1 Introduction

The Arctic Ocean is surrounded by permafrost, which is being degraded at an increasing rate under conditions of warming which are most pronounced in Siberia and Alaska (ACIA, 2004; Richte-Mengers et al., 2006). Permafrost thawing accelerates both river discharge (Lyon and Destouni, 2010), and carbon losses from soils (Finlay et al., 2006; Freeman et al., 2001; Guo et al., 2007). Siberian freshwater discharge to the Arctic Ocean is expected to increase with increasing temperatures (Savelieva et al., 2000; Semiletov et al., 2000; Peterson et al., 2002), which in turn may result in greater river export of old terrigenous organic carbon that has recently been documented to be fluvial exported to the ocean (Guo et al., 2004; van Dongen et al., 2008; Vonk et al., 2010a; Gustafsson et al., 2011). Rivers integrate variability in the components of the hydrometeorological regime, including soil condition, permafrost seasonal thaw, and thermokarst development, all the variables that determine atmospheric and ground water supply for the rivers and chemical weathering in their watershed. Thus, arctic rivers form an important link between the land and ocean carbon pools. In addition to serving as natural large-scale integrators of carbon-related processes occurring in their extensive drainage basins, the coastal export of the Great Siberian Arctic rivers (GSARs) of carbon and nutrients play a critical role in the biogeochemical regime of the Arctic Ocean evasion of CO_2 and CH_4 from river streams can significantly change the regional or even global carbon cycle (Kling et al., 1991; Richey et al., 2002; Bastviken et al., 2011). These authors cautioned that direct measurements of land-atmosphere CO_2 (and CH_4) exchange that ignore water-borne fluxes might significantly overestimate terrestrial carbon accumulation. A hypothesized climate-change-driven increase in terrestrial organic carbon inputs to the Arctic Ocean through permafrost thawing, increased river runoff, and accelerated coastal erosion could dramatically alter carbon budgets and biogeochemical cycles. While the fate and transport processes of terrestrial organic carbon across the Arctic land/ocean margin and consequent gas exchange are largely unknown, understanding them is critical to our understanding of environmental change on a time scale of human concern.

BGD

8, 2093–2143, 2011

Documented significant increases in the annual amplitude of Siberian river discharges and air temperatures in their watersheds over the past 30 years (Savelieva et al., 2000; Semiletov et al., 2000) have coincided with an increase in the amplitude of the seasonal cycle of atmospheric CO_2 and CH_4 in the north (Conway et al., 1994; IPCC, 2001), indicating a general increase in climatic variability. Therefore, a positive feedback loop could operate between the emission of CO_2 and CH_4 from northern ecosystems and changes in the atmospheric circulation and land hydrology, potentially resulting in greater fluvial export of terrestrial organic matter (OM). Changes in the export of terrestrial carbon will certainly affect biogeochemical cycling and carbon balance in the East Siberian Arctic shelf seas (Alling et al., 2010; Charkin et al., 2011; Romankevich and Vetrov, 2001; Sanchez-Garcia et al., 2011; Semiletov et al., 2005; Stein and Macdonald, 2004; van Dongen et al., 2008). Comprehending controlling processes and constructing budgets to calculate regional river input and shelf sea processing of the biogenic and anthropogenic materials requires comprehensive studies spanning over different seasons and years to not be mislead by such variability in the interpretation of a single year expedition.

Among the Siberian Rivers the Lena is considered to be the major source of total OM to the Arctic Ocean (Gordeev et al., 1996). Summer runoff from land, dominated by organic-rich soils, ice-complexes, and the mires of northern Asia, is an important source of carbon and nutrients to the shelf seas. Recent large-scale studies of terrestrial carbon in the ESAS water column has documented significant degradation of the terrestrial organic matter (e.g., Semiletov et al., 2007; Anderson et al., 2009; Alling et al., 2010; Vonk et al., 2010a; Sanchez-Garcia et al., 2011). Further, surface water from the shelf of the Laptev Sea, rich in dissolved OM, follows Gakkel Ridge towards Fram Strait (Anderson et al., 1998), possibly determining bacterial production over the Amerasian shelf and Arctic Basin (Wheeler et al., 1996; Opsahl et al., 1999). The Lena River is also considered to be the main sediment source for the Laptev Sea (Alabyan et al., 1995; Rachold et al., 2004) although the amount of suspended sediment delivered to the sea is still under some debate.

BGD
8, 2093–2143, 2011

Hydrometeorological analyses explaining the significant role of the Lena River-Laptev Sea system in the arctic freshwater budget can be found in Nikiforov and Shpaikher (1980), Zakharov (1996) and Semiletov et al. (2000). We view the Lena River as the seminal Siberian river because changes in Lena River hydrology play a significant role in ice and freshwater sources to the Transpolar Current through its effects on the freshwater budget of the Laptev Sea. The Lena River also forms a natural boundary between western and eastern Siberia in atmospheric circulation patterns, land hydrology, sea ice conditions, tectonic structure, and biological communities on the Siberian shelf (Semiletov et al., 2000, 2005).

This study is based on an extensive observational data set collected from seven field seasons in the Lena river system, extending from the headwaters near Ust-Kutsk to the Lena river plume in the recipient Laptev Sea. Studies include one expedition from late July to early August of 2003, the time of high water levels along the Lena River, from Ust'-Kut to the Lena Delta. Other data obtained in 1995, 1997, 1998, 2002, 2005, 2006 and 2008 are also discussed (Fig. 1). We present results of measurements of dissolved and particulate organic carbon and carbonate system components as a first approach to understanding the inter-annual and seasonal variability of the Lena River and its chemical signature in the adjacent waters of the Laptev Sea. We briefly discuss connections between the hydrochemical regime of the Laptev Sea, as influenced by river runoff, and atmospheric processes over the Arctic. The emphasis of this work is to summarize information about important biogeochemical fluxes, with a focus on carbon, that link runoff from the Lena River to the Laptev Sea, and further to the Arctic Ocean. Data on $p\mathrm{CO_2}$ and dissolved CH_4, obtained along the Lena River and in the adjacent part of the Laptev Sea, are considered. This information is critical for developing a general understanding of how the Arctic atmosphere-land-shelf system works.

BGD
8, 2093–2143, 2011

2 Data sets and methods

2.1 Field expeditions

Data were collected in different seasons before and after freeze-up over the period 1995–2008. The study areas visited in different years are presented in Fig. 1a, b, c. From late August to early September 1995 (Fig. 1a), surface water samples were taken onboard the motor vessel (MV) *Captain Ponomarev* from Yakutsk to the Lena River delta and Tiksi Bay in the Laptev Sea, by plastic bucket from the bow of the ship during slow cruising. The water samples were transferred immediately to hermetically sealed bottles (~500 ml) for gas chromatography (GC) measurements of dissolved CH_4 and total CO_2 (TCO_2). This route was repeated onboard the MV *Mekhanik Kulibin* in late August to early September 1998 (Fig. 1a). Shelf water influenced by Lena River runoff was sampled by Niskin bottles and measured onboard the hydrographic vessel (HV) *Dunay* in September 1997 (Fig. 1c). Some data obtained in the Laptev Sea onboard MV *Auga* (September 2005), small boat *Neptun*, MV *Kapitan Danilkin* (September 2006), MV *Mekhanik Kulibin* (late August–September 2008) and during winter expedition (April–May 2002) are also discussed (Fig. 1c). During flooding (late June to early August 2003) water sampling from the surface to the bottom was made by Niskin bottles from the upper stream down the Lena River to the Laptev Sea (Fig. 1b).

2.2 Salinity, nutrients and dissolved organic carbon

Chlorinity (titrated, Cl), salinity (S), phosphate (P-PO_4), nitrate (N-NO_3) nitrite (N-NO_2), and total dissolved N and P in water samples were determined by traditional oceanographic techniques prescribed by Ivanenkov and Bordovsky (1978). Total (TOC) and dissolved organic carbon (DOC) were determined using samples sealed in glass tubes by the Shimadzu TOC-5000 high-temperature catalytic oxidation technique in the laboratories at the University of Alaska, Fairbanks.

BGD
8, 2093–2143, 2011

2.3 Particulate organic carbon (POC) and nitrogen (PON)

During flooding (late June to early August 2003) the suspended particulate matter (PM) dynamics and the composition and isotopic signatures of its organic material components (POC and PON) were measured from the upper stream down the Lena River to the Laptev Sea (Fig. 1b). Concentration and isotopic signatures of POC and PON were measured at the University of Alaska Fairbanks using a Finnigan isotope ratio mass spectrometer (IRMS) (Schell et al., 1998; Guo et al., 2004; see website at http://www.uaf.edu/water/ASIF/ASIF.html).

2.4 pH

Two different techniques were used for pH measurements. pH measurements were made in situ: an open electrochemical cell was used for surface samples and for winter measurements prior to and including 1997 (Semiletov, 1999a). A closed electrochemical cell, which avoided CO_2 leakage into the atmosphere, was used to measure pH in samples taken from sites in all seasons after 1997. NBS commercial standard buffers were used to check the Nernst slope of the electrode pairs. Because natural variability in the Arctic river and shelf water samples is large (up to 1 pH unit), we consider the pH difference of a few 10^{-2} units between values of pH measured in open and closed pH cells to be negligible.

2.5 Total alkalinity and $p\mathrm{CO_2}$

Samples for measurements of total alkalinity (TA) were obtained following Dickson and Goyet (1994) and analyzed within 12 to 24 h of collection by direct indicator titration in an open cell using 25 ml of water with 0.02 N HCl according to Bruevich's method (Ivanenkov and Bordovsky, 1978). Comparison of TA determination by Bruevich's and Edmond's methods (Dickson and Goyet, 1994) showed that the difference in TA did not exceed 0.02 mmol kg^{-1}. This difference is ignored here because the error in calculating partial pressure of CO_2 (pCO_2) is influenced mainly by the uncertainty in the measured pH value (±0.01 pH). The pCO_2 was computed from pH and TA, and from pH and TCO_2 according to the methods advocated by UNESCO (1987). We used the equation of Weiss (1974) to represent CO_2 gas solubility as a function of temperature and salinity, and the equations of Millero (1995) for temperature and salinity (chlorinity) dependence of the apparent dissociation constants for boric and carbonic acids in freshwater and seawater as determined by Lyman and Meerbach et al. in UNESCO (1987). To calculate pCO_2 values in freshwater, we applied apparent constants for dissociation of carbonic acid advocated by Millero (1979, 1981), thermodynamic constants from Plummer and Busenburg (1982), and individual ion activity coefficients from Stumm and Morgan (1981). Agreement among results of all applied techniques was good with the pCO_2 difference not exceeding 1%. Detail description for all measurements and calculations can be found elsewhere (Pipko et al., 2002, 2011; Semiletov et al., 2007).

2.6 TCO_2 and CH_4

To measure TCO_2 we used a gas chromatograph, TSVET-530 or LKHM-80MD, with a Poropac T (1.5 m, 80–120 mesh) and a flame-ionization detector (FID) run isothermally at 30 °C with hydrogen carrier gas; a stripping GC technique similar to that described in Weiss (1981) was used. The calibrations of TCO_2 were based on three standard solutions of Na_2CO_3 with concentrations of 0.73, 1.02, and 1.99 mM that were prepared gravimetrically in fresh, distilled water. Conversion of CO_2 to CH_4 after the Poropac column was done in a Ni-catalyst column (14 cm Chromaton, 80–100 mesh, coated by Ni) at 400 °C (Semiletov, 1993). The measurements are reproducible to within ±1–2%. The concentration of dissolved CH_4 was also determined by FID. Water for gas analysis was collected in hermetically sealed glass bottles from just below the sea or river surface in the manner recommended by Dickson and Goyet (1994) for CO_2 system study. Concentration of CH_4 in the equilibrated gas phase (C_G) was determined by a GC head-space technique. The concentration of dissolved CH_4 (C_L) was calculated using the main static head space equation of Vitenberg and Ioffe (1982): $C_L = C_G(V_G/V_L + K)$, where V_L and V_G are volumes in the gas (G) and liquid (L) phases of the closed head-space system with thermostat set to ambient, and K is a gas partitioning coefficient. Calibration was done with clean CH_4 using a precision multivalve positioned at ambient temperature. The total precision of this technique, which was used until 2003, varied between 3–5%; variation was usually due to instability in shipboard electricity (Semiletov, 1993; Semiletov et al., 1996a). High-precision measurements of dissolved CH_4 were done in September 2005, 2006, and 2008 using a Micro-Tech-8160 GC equipped with FID. For calibration in 2005, 2006, and 2008 we used certified CH_4 gas standards in a balance of air (Air Liquide, USA). This technique has been successfully used by Shakhova et al. (2005, 2007a, b, 2010a, b) and Shakhova and Semiletov (2007). Samples stored more than 4 h before measuring dissolved CH_4 and TCO_2 were treated with mercuric chloride to poison biological activity.

3 General description of the Lena River Basin

The Lena River originates near Lake Baikal from a large ($\sim 2.5 \times 10^6$ km^2) drainage basin within 53–71° N and 105–141° E, which is located in one of the most remote areas of the Eurasian continent and contains a large variety of geological features. The Lena River basin is phytogeographically an area of transition among various Siberian landscapes: boreal and northern taiga, forest tundra, shrub tundra, open-woodland tundra, and semi-desert tundra. The Lena watershed area exceeds the entire area of the ESAS ($\sim 2.1 \times 10^6$ km^2 including the Laptev and East Siberian, and Russian part of the Chukchi Sea), which in turn is the broadest and shallowest shelf in the World Ocean. The ESAS alone constitutes almost 20% of the total area of the Arctic Ocean, with a mean depth of only 50 m. The changing fresh water and biogeochemical signal from the Lena's vast drainage area in the ESAS can be considered as an indicator of ongoing changes in the East Siberia (Savelieva et al., 2000; Semiletov et al., 2000; McClelland, 2011).

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

BGD

8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

The delta of the Lena River occupies 28.5×10^3 km^2 making it the second largest in the world (after the Mississippi River) and the largest delta in the Eurasian continent. About 30 000 lakes are located in the delta, 90% with a typical size of ~0.25 km^2 and only 100 lakes with surface area >10 km^2. According to official terminology, the delta begins downstream of Stolb Island (Fig. 1a). Following Antonov (1964) for 1936–1950s data and the Tiksi Hydromet data for 1953–1990s (Sidorov, 1992), the Bykovskaya branch (Bb) of the mouth receives about 24% and 28% of the total discharge during winter low water and summer high water, respectively, while the Trofimovskaya branch receives about 70% and 54%, and the Tumatskaya and Olenekskaya branches receive about 3% and 8–10%, respectively. According to Antonov (1964) and Ivanov (1970), the Bb hydrological regime reflects all important features of other branches of the Lena River delta. Because the Bb has been the most accessible and investigated, we collected our main set of samples in this channel in different seasons (Fig. 1a, b).

The Lena basin is generally located in the continuous permafrost zone where the frozen layer depth varies from 50 m to 1500 m. In the delta area the permafrost extends down to 600 m, though large lakes and rivers can be underlain by taliks extending through permafrost (Grigoriev and Kunitsky, 2000). It is assumed that under the Laptev Sea the depth of the offshore layer of relict permafrost varies between 50 and 200 m. Note that estimation of the subsea permafrost distribution is mostly based on modeling, but some geophysical and borehole's data show that the subsea permafrost is the most fragile component of the modern cryosphere because mean temperature for the upper 100 m sediment layer is rougly $-1\,^{\circ}$C, while it is $\sim -12\,^{\circ}$C onshore (see discussion in Shakhova et al., 2010a, b; Nicolsky and Shakhova, 2010; Rachold et al., 2007). A vast amount of buried OM with an average 3–5% C by weight is presently reentering biological cycling due to thawing and erosion of onshore and offshore permafrost. The upper 100 m of permafrost in Siberia (tundra and northern taiga, 9.4×10^6 km^2) contains no less than 9400 Gt (1 Gt = 10^{15} g) of organic carbon (assuming low mean OC concentration equal 0.5% w/w) that could be available for biogeochemical cycling through permafrost degradation, including coastal erosion (Semiletov, 1999a, b). Taking into

BGD
8, 2093–2143, 2011

account that ~90% of ESAS was land that was flooded by the sea during transgression, we may assume that the upper 100 m shelf sediment layer itself contains at least 1800 Gt of organic carbon. This reservoir also consists of ESAS hydrate deposits estimated to hold ~540–750 Gt of CH_4 with an additional 2/3 (~360–500 Gt) trapped below as free gas (Shakhova et al., 2010a). Thus, the Lena River serves as a pathway to relocate terrestrial organic carbon between the land and shelf carbon megapools. Additionally, bottom erosion and subsea talik formation (Romanovskii and Hubberten, 2001; Shakhova and Semiletov, 2007; Dudarev et al., 2008) can be a significant source of old carbon (predominantly in the form of CH_4 and CO_2) to the water column.

The water balance of the Siberian Rivers situated in the permafrost region differs from that of rivers in other regions because the upper surface of the permafrost (permafrost table) beneath the seasonally thawed layer is a water-impermeable sheet that influences land hydrology and hydrochemistry. The permafrost table depth varies from 10 to 10^2 cm north of the Arctic Circle, but in southern mountainous areas discontinuous permafrost (permafrost islands) may be from 10^3 to 10^4 cm deep. Therefore the regime of groundwater flow is significantly different for rivers situated in different permafrost environments, and also different between rivers in any permafrost environment and rivers in non-permafrost environments (van Dongen et al., 2008; Guo et al., 2004; Semiletov et al., 2000).

4 Results and discussion

4.1 Fluvial transport and sedimentation in the Lena River delta and adjacent seas: river-derived PM and POC

Boucsein et al. (2000) argue that at the beginning of the Holocene a significant change in composition of sediment OM (increase of fresh-water alginite and immature plant material) on the Laptev Sea continental slope was due to increased Lena River discharge. Alternatively, Bauch et al. (2001) believe that the increased Holocene deposition of OM in the Laptev Sea is mainly the result of coastal erosion due to the sea level

BGD
8, 2093–2143, 2011

transgression. Therefore it is important to study the role of the Lena River and coastal erosion in different summer months when the major water and solid discharges occur.

Our observations of PM distribution along the Lena River from the upper stream (Ust'-Kut) in late June to August of 2003, mid-stream (Yakutsk) in late August to early September of 1995 and 1998, and down to the Laptev Sea (Fig. 1) demonstrate that almost all riverine PM settles in the delta, even during spring/summer high river discharge time as observed in June–July 2003 (Fig. 2a, b, c). PM concentration increased from a low (10–15 $\mathrm{mg\,l^{-1}}$) in the lower river to as much as 30 $\mathrm{mg\,l^{-1}}$ in the Bykovskaya channel of the delta, but decreased to 5–10 $\mathrm{mg\,l^{-1}}$ in the channel outlets (Fig. 2). Note, that two stations (encircled area in Fig. 2) were accomplished in the Bykovsky channel in early August in the beginning of the "second flooding wave". Both August stations exhibit a doubling of the PM concentrations compared with the survey accomplished one week earlier. The observed PM increase in the delta channels may also be related to the coastal erosion, which is common in this area (Grigoriev, 1993). The mean PM content we measured in the river was 19.4 $\mathrm{mg\,l^{-1}}$, about half the mean value (38.5 $\mathrm{mg\,l^{-1}}$) reported by Romankevich and Vetrov (2001) and the mean (34 $\mathrm{mg\,l^{-1}}$) from Gordeev et al. (1996). Both used the data obtained by the Soviet Union Hydrometeorological Service. The difference may be related to the use of filters with non-standard, most likely smaller, pores in the latter studies compared to the now canonical Whatman GF/F borosilicate filters.

Values of δ^{13}C in river POC ranged between −30‰ and −25‰ with a mean value near −27‰. A similar range of POC δ^{13}C values was reported by Rachold and Hubberten (1999) for the Lena, Khatanga, and Yana basins. The δ^{13}C values of the organic fraction of the surface bottom sediment, measured in the delta and the southeastern part of the Laptev Sea during September 1997, show a terrestrial origin for the OM. These results agree with Rachold and Hubberten (1999) who found nearly constant δ^{13}C values for particulate OM throughout the river, with an average of -27.0 ± 0.8‰, reflecting the dominant contribution of C_3 plants. Similar values of δ^{13}C were found in the Yenisey estuary (Kodina et al., 1999) and Lena estuary (McClelland et al., 2008).

BGD
8, 2093–2143, 2011

Reasons for the δ^{13}C variability in POC are discussed briefly by Rachold and Hubberten (1999), though clarification of this issue will require additional study. Note, that the δ^{13}C value (−27.70‰) is constant in Neelov Bay of the delta and close to values (−27.16 to −27.54‰) measured in the sediments of the Laptev Sea between Big Lyakhovsky Island and Cape Svyatoy Nos where coastal erosion dominates (Semiletov, 1999b).

Using the mean PM concentration of 20 mg l^{-1} and an annual river discharge of 525 km^3 we calculated the "mean" solid discharge to be 10.5 Tg (1 Tg = 10^{12} g) delivered through the delta channels. Annual discharge of POC may be equal to 0.38 Tg if we use a mean POC value of 0.75 mg l^{-1}, which was obtained in 2003 along the Lena River during flooding (moderate or high estimates). If we accept Lisytsin's (1994) statement concerning the precipitation of 85–95% of total PM (and POC) on the marginal "filter", then only about 1 Tg of PM, and 0.03–0.04 Tg of POC reaches the Laptev Sea from the Lena River. Similarly, in summer and fall the solid discharge of other major East Siberian Sea Rivers, the Indigirka and Kolyma, is also limited by the near-mouth areas (Ivanov and Piskun, 1999). Note, that the OM exported by the eastern GSARs (Lena, Indigirka, Kolyma) and local coastal erosion, despite high bulk radiocarbon ages, are less degraded than their western Siberian counterparts (Ob and Yenisey), which is consistent with increasing permafrost and a shorter annual thaw period in eastern Siberia compared with western Siberia (Guo et al., 2004; Gustafsson et al., 2011; van Dongen et al., 2008).

A second Lena River "flooding wave" in summer of 2008 brought unusually high amount of PM/POC with light δ^{13}C signature to the Laptev Sea which was dispersed further north of the Lena Delta (Sanchez-Garcia et al., 2011). At that time, contribution from the coastal erosion was small, because low winds/waves did not removed the eroded material from the foreshore zone to the sea (Charkin et al., 2011). Thus, the partitioning between fluvial and "coastal erosion" POC input to the sea can vary significantly from year-to-year depending on hydrometeorological conditions over land and ocean.

BGD
8, 2093–2143, 2011

The spatial trends of $\delta^{13}C_{org}$ in the bottom sediment can be used to quantitatively estimate the contribution of terrestrial organic matter (CTOM) to the ESAS sediment. Following Walsh at al. (1989), the amount of organic carbon (OC) derived from terrestrial end-member $\delta^{13}C_{ter}$ (terrestrial C) can be calculated from the data as

$$CTOM(\%) = (\delta^{13}Co - \delta^{13}C_{mar}) \times 100 / (\delta^{13}C_{ter} - \delta^{13}C_{mar}),$$

where "o", "mar", and "ter" refer to the $\delta^{13}C$ values of observed, marine, and terrestrial sediment. If we take the two end members to be a $\delta^{13}C_{ter}$ of −27‰, typical of higher plants, and a $\delta^{13}C_{mar}$ of −21‰, typical of phytoplankton (Walsh et al., 1989; Naidu et al., 2000), then the CTOM values for the East Siberian Sea: Western geochemical area and the Eastern area (bounded by CTOM = 70%) become 86% and 52% of terrestrial OC, respectively (Fig. 3).

Calculations made for the entire ESAS indicate that there is a significant amount of terrestrial OC stored within sediments, especially in the near shore zone most strongly influenced by coastal erosion: between the Dmitry Laptev Strait and the Kolyma mouth, the OC is almost all of terrestrial origin (from 81% to 100%, mean CTOM = 93%). In contrast, the sediments underneath transformed Pacific – origin water (the Eastern area) are almost half of marine origin (Fig. 3). That result is agreed well with n-alkanes measurements in the surface sediment OC (Vetrov et al., 2008) and a three end-member isotopic mixing model for POC applied along the Kolyma paleo-river transect (Vonk et al., 2010a) which revealed that the proportion of OC derived from coastal erosion was substantial (51–60%).

The PM data obtained in the Dmitry Laptev Strait where the river PM signal is negligible show that "new production" is formed from the old terrigenous carbon with a typical terrestrial signal of $\delta^{13}C_{ter} < -26.5‰$. Thus the river OM discharge has probably no direct influence on marine productivity, while coastal erosion and consequent degradation of "fresh" old terrestrial organics builds up pCO_2 value up to 1500–2000 µatm in summer, and 5000 µatm in winter and plays a significant role in biogeochemical processes especially in the south-eastern area of the Laptev Sea, and western area of the East-Siberian Sea where coastal retreat is highest (Pipko et al., 2005, 2008, 2011; Semiletov, 1999a, b; Semiletov et al., 2004, 2007; Anderson et al., 2009, 2011; Alling et al., 2010). Detail discussion for dynamics of the carbonate system in the Lena-Laptev Sea can be found below (Sect. 4.2).

During August–September, when the river discharge is low but the rates of coastal erosion are highest, the mean PM concentration (24.2 mg l^{-1} in the surface layer and 25.4 mg l^{-1} in the near bottom layer, Semiletov et al., 2005) obtained over the western part of the ESAS inner shelf (>40 m in depth) is several times higher than it was reported for the Lena river – Laptev shelf system during the "surge freshet" (Pivovarov et al., 1999). Note, that the highest PM concentrations were observed in the Dmitry Laptev Strait (>100 mg l^{-1}) which is outside the area of direct river sediment input (Dudarev et al., 2003). The finding of anomalously high concentrations of benthic organisms (up to 100–200 g C m^{-2}) at the coastal bottom depressions of the Laptev Sea (Gukov et al., 1999) could be associated with near-shore accumulation of eroded old organic carbon.

Several studies show that transport of coastally eroded material into the Laptev and East Siberian seas ranges between 40–70 Tg (Are, 1999; Grigoriev and Kunitsky, 2000)" with a mean organic carbon concentration of 3%. Annual transport of eroded terrestrial carbon onto the shelf may therefore range from 1.2 Tg to 2.1 Tg. The upper limit of this range is close to our previous estimate made for the Laptev and East Siberian seas which gives a higher "mean" annual POC flux value of 2.5 Tg (Semiletov, 2001) which is a value about two orders of magnitude higher than the Lena River POC discharge into the sea. Higher annual estimation (∼4 Tg) was made by Rachold et al. (2004).

4.2 Processes controlling the distribution and loss of fluvial POC across the ESAS

The East Siberian Sea is strongly impacted by the Lena River plume (Anderson et al., 2011; Pipko et al., 2008, 2011; Semiletov et al., 2000; Shakhova and Semiletov, 2007;

BGD
8, 2093–2143, 2011

Alling et al., 2010). However, the fate of the Lena CTOM in POC plume across the ESAS and its contribution to sedimentation was not studied yet. To illustrate anomalous export of terrOM in the ESAS we show the integrated plume of PM and CTOM in POC for the period 2003–2007 (Fig. 4) obtained east of the Lena Delta. These observations support the hypothesis of a dominating role of coastal erosion (Semiletov, 1999a, b) in the ESAS sedimentation and dynamics of the carbon/carbonate system. It can be seen that the PM and CTOM/POC plume from the Lena is limited by the narrow nearshore zone where most of the Lena River burden settles. The pattern also shows a negligible direct influence of the Lena transport of PM into the East Siberian Sea.

The Quartz/Feldspar (Q/FS) ratios in the western and eastern East Siberian Sea are the same (Q/FS = 0.26), while ratios typical of the Lena River are 10 times higher (between 2 and 2.3) (Serova and Gorbunova, 1997). This evidence also indicates an insignificant direct influence of Lena River transport of PM into the East Siberian Sea. Note that in summer-fall the solid discharge of the major East Siberian Rivers, Indigirka and Kolyma, is also limited by the near-mouth areas (Ivanov and Piskun, 1999). Then we can argue that transport of the eroded material (Semiletov, 1999ab) plays major role in accumulation of carbon in this part of the Arctic Ocean. Note that only in summer/fall of 2008 we obtained a significant contribution of Lena POC burden to the adjacent part of the Laptev Sea and western east Siberian Sea (Sanchez-Garcia et al., 2011), because of the abrupt second summertime flooding wave and low wind condition preventing removal of eroded carbon from foreshore to the sea (Charkin et al., 2011).

All the geochemical data obtained in the summertime expeditions (1999–2007, except of 2008 when anomalously high the Lena River solid discharge was obtained: see Sanchez-Garcia et al., 2011; Charkin et al., 2011) clearly show that the depositional environment in the Lena River prodelta and the Buor-Khaya Gulf is dominated by coastal erosion rather than by riverine input. This conclusion agrees well with available CN stable isotope data, C/N ratios, and the distribution of biomarkers (Semiletov et al., 2005; Vetrov et al., 2008; Karlsson et al., 2011). Thus, we argue that in the

BGD
8, 2093–2143, 2011

1995–2005 period, the Lena River solid discharge played a minor role, compared with offshore transport of eroded material, in accumulation of carbon in this part of the Arctic Ocean; this conclusion also supports the conclusion of Bauch et al. (2001) and Vonk et al. (2010a).

Our studies to date show that terrOM entering sub-Arctic Baltic and Eurasian Arctic seas follows continent-scale trends in molecular and isotopic composition. *Sphagnum* is a key contributor to the pre-aged (1000s of ^{14}C years) terrOM in these coastal waters; the greatest *Sphagnum* contribution but the youngest terrOM occurs toward the west (Vonk and Gustafsson, 2009; Vonk et al., 2010a). There was also rapid degradation during settling and in the surface sediment (Sanchez-Garcia et al., 2011; Vonk et al., 2010a). A simple box model was parameterized with measurements of advective river input, settling fluxes, and advective export, and was solved for degradation (Gustafsson et al., 2000; van Dongen et al., 2008). The model was run for both individual biomarkers, bulk POC and bulk DOC. Rapid terrPOC degradation was constrained (65% during the 5-day box transit). This translated into a degradation rate for terrPOC nearly 20 times more rapid than for terrDOC, which makes both pools equally important for the total terrOM degradation. Similar trends for POC-biomarkers and degradation indexes between the Kalix-Baltic and GSARs systems suggest that the early processing may be similar on the Eurasian Arctic shelf (Vonk et al., 2008, 2010b; Gustafsson et al., 2011). Taken together, all recent benchmark studies of the current composition of terrestrially exported POM suggest distinguishing continent –scale trends in molecular composition of the OM across the west-east Eurasian shelf seas, which reflects both differences in vegetation and climate (Guo et al., 2004; Gustafsson et al., 2011; van Dongen et al., 2008; Vonk et al., 2010a, b). If the climate in the ESAS region becomes more like the current state in the west Siberian region, these results would predict a greater degree (comparing with western Siberia) of decomposition of the old terrestrial OM released by the coastal erosion and the Lena and others eastern GSARs and thus greater remineralization and release as CO_2.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

BGD

8, 2093–2143, 2011

4.3 Dynamics of the carbonate system in the Lena River – Laptev Sea system

4.3.1 The carbonate system in the river and near-shore zone

In summer 1995, we began a study of the carbonate system and dissolved CH_4 in the Lena River delta and adjacent shelf waters (Fig. 1). In general we sampled the surface layer, though in 1996–1998 and 2006 vertical sampling sections were also conducted. We consider the summer surface chemical data from the river to be representative of the whole because measurements of temperature, conductivity, dissolved oxygen, colored dissolved organic carbon (CDOM), TOC, pH, and TCO_2 throughout the major water column (except of deeps) were the same. The total carbon ($TC = TCO_2 + TOC$) transported by the Lena River is a significant contribution to the sea, especially during flood periods. The fate of this carbon pool, whether consumed more or less rapidly in the adjacent sea or accumulated in the coastal zone, is one of the important questions posed by this system.

Summer

To understand the carbon cycle in the Lena River we carried out a shipboard investigation along a 1700 km section from Yakutsk to Tiksi on the Laptev Sea coast. During a 5-day voyage, in late August to early September 1995, 41 sites were surveyed (Fig. 1a). At that time, the surface waters of the Laptev Sea near the delta were strongly freshened by the river discharge. The major components of the carbon cycle (TCO_2, TOC, pH) and silicate (an indicator of continental crust weathering) were sampled (Table 1). Because the river includes water entering from a basin that extends throughout almost all of Yakutia, the signature from the major tributaries, the Aldan and Viljuy rivers, can be identified.

TCO_2 varies inversely to TOC concentration down the Lena River (Figs. 5, 6). In the coastal waters of Tiksi Bay (sites 40 and 41) TCO_2 and TOC concentrations increase drastically. This increase in TOC, TCO_2, and TC values is consistent with the maximum primary production (432 mg C m^{-3} d^{-1}) and mesozooplankton biomass (890 mg m^{-3}) measured in the Lena River – Laptev Sea system in the same month (September 1991) (Sorokin and Sorokin, 1996). Therefore Tiksi Bay is a summer biogeochemical oasis, where the estuarine environment replaces the winter sea environment when river discharge is low.

Highest TOC concentrations (Table 1) were found in the Lena mid-stream between the inflow of the Aldan River and the Viljuy River (Figs. 1a, 5). The TC value increases to 0.3 mM (~0.2 mM as TCO_2, ~0.1 mM as TOC) due to inflow of the Viljuy River in comparison to a TC of 0.2 mM (~0.0 as TCO_2, ~0.2 mM as TOC) contributed by the Aldan River. The plot of TCO_2 and TOC shows high variability: (1) TCO_2 ranges from 0.63–1.07 mM (mean = 0.85 mM) from Yakutsk to Stolb Island, to 0.84–1.38 mM (mean = 1.06 mM) in the delta and Tiksi Bay; (2) TOC decreases from 0.39–0.93 mM (mean = 0.59 mM) from Yakutsk to Stolb Island, to 0.38–0.53 mM (mean = 0.47 mM, except at site 40) from Stolb Island to Tiksi (Fig. 6). In general, the distribution of TCO_2 and TOC in river waters, excluding Tiksi Bay, shows a negative correlation ($r = -0.60$).

Comparison of our results obtained along the Lena River and in the nearshore zone near the Lena delta at the same time (September) in 1995 and 1998 with the data obtained by Cauwet and Sidorov (1996) in 1991 within the framework of the Russian-French expedition SPASIBA-2 demonstrates significant inter-annual variability in mean values of total inorganic carbon (CO_2), TOC, and their sum (TC), Table 2. We suggest that this variability is determined by changes in land hydrology which cause differences in the Lena discharge (Pipko et al., 2010). About one month is required for water to travel from Yakutsk to the Laptev Sea. For example, the mean Lena discharge (18 800 m^3 s^{-1}) in August 1995, was about 89% of the discharge in August 1998 (21 100 m^3 s^{-1}), while the mean TC value in 1998 was 87% of the TC value in 1995. Hence, this appears to be a dilution effect. Increasing the Lena discharge causes opposite effects on dissolved organic and inorganic carbon: TOC concentration increases, while $_2$ concentration decreases (Pipko et al., 2010). This phenomenon is also observed in Kalrix river in sub-Arctic Scandinavia (Ingri et al., 2005).

BGD
8, 2093–2143, 2011

Cauwet and Sidorov (1996) also found a positive correlation between TOC values and river discharge. The mean TCO_2 in the river from Yakutsk to Stolb Island (where the major Lena stream is separated into delta channels) was 0.65 mM in 1998, about 76% of the mean TCO_2 obtained in 1995. We found a high negative correlation (–0.91) between TCO_2 values and river discharge. In the river system the TC distribution is quasi-homogeneous with a total mean of 1.48 ± 0.03 mM (except for site 40 which exhibits an extremely high TOC), while TOC and TCO_2 changed in an opposite manner (Fig. 6). This indicates that transformation of organic carbon into mineral carbon in the aquatic environment, and mineral carbon into the organic form in the Lena River watershed, can be considered quasi-equilibrated processes. The mean pH_{25} was 7.83 and 7.81 in the delta and coastal waters of the Laptev Sea, respectively; the value is similar in the middle and downstream waters of the Lena. Relatively high pH_{25} values, up to 8.01 (site 18), in the lower river, are similar to the pH_{25} values measured near outlets of small streams draining from lakes in the taiga-tundra zone of the Kolyma lowland (Semiletov et al., 1996a, b).

The interannual difference in the hydrological regime is also reflected in the temperature gradient of the river. In early September 1998 the gradient was 12 °C from 18.6 °C near Yakutsk to 6.6 °C in Tiksi Bay, compared to a 7 °C change in 1995. The larger temperature gradient in 1998 resulted from greater cooling in Tiksi Bay, 6.6 °C in 1998 vs. 10.4 °C in 1995. An increase in river discharge is in agreement with an increase in the horizontal gradient of the river's surface temperature between Yakutsk and Tiksi. This parameter can be used as an additional indicator of inter-annual and long-term thermal changes across the Lena (and other river) watersheds. A decrease of TCO_2 and TOC in September 1998 relative to September 1995 could be the result of a high supply of snow and glacial melt water from mountain areas in the Lena River watershed.

The fate of organic-rich Lena River water in the Laptev Sea, when plotted against salinity for measurements from September 1997 and for data collected by Cauwet and Sidorov (1996) in 1991, indicates a similarity between mean values of TCO_2 and TOC (0.58 mM vs. 0.60 mM, respectively) near zero salinity (Fig. 7). These values reflect

BGD
8, 2093–2143, 2011

the contribution from all rivers that discharge into the Laptev Sea (Lena, Khatanga, Yana, Anabar). TCO_2 values obtained in September of 2003 and 2004 in the East-Siberian Sea and extrapolated to zero salinity were 0.52 mM and 0.50 mM, respectively (Semiletov et al., 2005). Thus, assuming the melt water signal is negligible over the shallow East Siberian Sea shelf at the end of hydrological summer (Anderson et al., 2009), we can state that an integrative TCO_2 signal from the Lena and other rivers flowing in the Laptev Sea and further east is slightly high compared with the signal from rivers that discharge into the East-Siberian Sea.

The mean pCO_2 value increased from 538 µatm in the middle and lower portions of the river to 592 µatm in the delta and nearshore sea. This increase is caused by a corresponding increase of TCO_2 that dominates over the temperature shift in the carbonate system. These results generally agree with those measured in the mouths of the Ob and Yenisei rivers (Makkaveev, 1994), and in arctic Alaska rivers (Kling et al., 1991).

A simple calculation shows that only the Lena River annually brings to the sea a significant amount of dissolved inorganic and organic carbon; if the mean $TCO_2 = 1$ mM, TOC = 0.5 mM, TC = 1.5 mM (~18 mg l^{-1}), and $W = 525\,km^3\,y^{-1}$, then total carbon entering the sea would be almost 10 Tg C y^{-1}. This suggests that the total carbon added by Lena River runoff over $45 \times 10^3\,y^{-1}$ is equal to the total accumulation of inorganic carbon in the Arctic Ocean, 450 Gt C. Because of the low POC level in the Arctic Ocean, we assume that total $TCO_2 \approx$ TC. Therefore, a huge amount of carbon (~100 Gt C in mineral and organic forms) was transported during the Holocene (~ 10×10^3 y) from land to the Arctic Ocean by then Lena River and then to the North Atlantic. Understanding the proportions of "primary river carbon" that are redistributed to the main carbon pools is an important problem that is starting to be addressed (e.g., Stein and Macdonald, 2004; Alling et al., 2010).

Winter

In winter of 1995 pCO_2 was 1267–1579 µatm in Gerasimovskaya and Sinitsina channels, 1045–1500 µatm in Neelov Bay, and 2140–5800 µatm in Tiksi Bay due to an increase in TCO_2 and a decrease in pH (Semiletov et al., 1996b). Maximum pCO_2 values were found in May when winter OM is oxidized and CO_2 accumulates beneath the ice cover (Semiletov et al., 1999b). May is a period of spring phytoplankton blooms when dissolved CO_2 is removed from ocean surface waters by photosynthesis, but here the winter accumulation primarily determines the spring concentration of CO_2. Data obtained in April–May 2002 in the Buor-Khaya Gulf of the Laptev Sea, adjacent to the eastern part of the river, show dramatic pCO_2 changes throughout the water column from summer (Fig. 8a) to winter (Fig. 8b), when fast ice thickness exceeds 2.0 m. In winter, when OM decomposition dominates, pCO_2 was greater than 4000 µatm near the bottom. Data show that supersaturation beneath the sea ice is a principal feature of the carbon cycle in the Arctic Siberian seas (Semiletov, 1999a; Semiletov et al., 1996a, b, 2004) and in the central basin of the Arctic Ocean (Semiletov et al., 2007). Wintertime CO_2 and CH_4 accumulation beneath the ice was also found in north Siberian lakes (Semiletov, 1999b).

4.3.2 The influence of Lena River on the carbonate system in the East Siberian Shelf Seas

Here we present CO_2 data that were obtained in the Laptev Sea, which is influenced strongly by inflow of the Lena River (Figs. 9, 10).

East of the delta

Year-round study of the CO_2 system in the Lena River-Laptev Sea system shows that river waters are a source of CO_2 into the atmosphere during all seasons. Likewise, long-term hydrochemical investigations by the Russian Arctic and Antarctic Research

BGD
8, 2093–2143, 2011

Institute (Rusanov and Shpaikher, 1979) and a continuing study by the Tiksi Hydrometeorological Service show that dissolved oxygen concentrations are inversely proportional to pCO_2 concentrations obtained in our data. The measured concentrations of dissolved CO_2 and oxygen are a result of OM oxidation and interaction between the physical and biological processes of cooling or warming, photosynthesis and respiration as well as mixing of different waters.

The ΔpCO_2 ($\Delta pCO_2 = pCO_2^{sw} - pCO_2^{air}$) data show that the surface layer of the eastern Laptev Sea is supersaturated in CO_2 relative to the atmosphere (Fig. 9); the highest supersaturation was found near the delta and over the Vasilievskaya-Semenovskaya shoals which are characterized by high rates of bottom erosion and elevated values of POC (Dudarev et al., 2008), perhaps a result of upwelling of bottom water enriched in CO_2. Because the uptake of CO_2 by photosynthesis is relatively high only in the delta surface waters of the Siberian rivers (in the Lena River up to 0.1–0.3 g C m^{-2} d^{-1}) and decreases 10–100 times toward the shelf edge (Sorokin and Sorokin, 1996), we assume that the level of CO_2 saturation is not strongly affected by photosynthesis especially in the low-transparency water strongly impacted by the Lena River (Pipko et al., 2011; Semiletov et al., 2007). Available data show that the eastern Siberian coastal zone, influenced by river run-off and coastal erosion, is a source of atmospheric CO_2 during summer and winter, whereas areas of the Laptev Sea remote from the coastline tend to be sinks in summer (Semiletov, 1999a, b; Semiletov et al., 2007; Pipko et al., 2008, 2011; Anderson et al., 2009, 2011). Therefore, the CO_2 exchange between air and sea exhibits a spatial-temporal mosaic pattern across the different Arctic seas.

The data show that the sea surface layer influenced by the river is 2–3 times higher than saturation in CO_2 (Semiletov et al., 1996a, b). The value of pCO_2 near the entrance of the Kolyma River in the East Siberian Sea was 716–1779 µatm in fall 1994 which is close to the range obtained in the same area in the summers of 2003 and 2004 (Pipko et al., 2005, 2008). Data obtained in fall 1995 show that not far from the mouths of the Ob and Yenisei rivers the pCO_2 of the Kara Sea surface waters was higher than that of water farther offshore (Semiletov et al., 1996a, b). These data show that the

BGD
8, 2093–2143, 2011

coastal zone exhibits higher pCO_2 value compared with rivers themselves. The combined effect of CO_2 export by rivers and aerobic oxidation of coastline-eroded carbon are responsible for that increase (Semiletov, 1999a, b).

North of the delta

The September 2006 vertical transect from the Lena Delta to the north illustrates how far the Lena River signal is propagated (Fig. 10). It has been shown that the relatively fresh and warm (<2 °C) riverine plume is characterized by high silicates and normalized TA values (nTA), relative to the typical Atlantic water layer in the Arctic Ocean, with $S = 35$), while total dissolved phosphorus (P_{tot}) and total dissolved nitrogen (N_{tot}) are almost completely depleted in the Lena plume at the end of biological summer. Vertical fluxes yield a mosaic picture of CO_2 sources and sinks, while the northern periphery of the Lena River plume (up to 80° N) is a source of CO_2 to the atmosphere (Semiletov et al., 2007). Measurements of CO_2 turbulent flux taken in September of 2005 above open water over the Laptev Sea shelf and slope ranged between the positive (evasion) and negative (invasion) values of $+1.7\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ and $-1.2\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ (Semiletov et al., 2007). Comparing distribution of CO_2 fluxes with surface temperature and salinity shows that warmer and fresher water, which is probably the Lena River plume, acts as a source of atmospheric CO_2, while relatively colder and saltier water near the ice edge is a sink (Semiletov et al., 2007).

Ice-tethered observations made in the central Arctic Ocean by the Russian North Pole-33 drifting station in the summer of 2005 show that values of pCO_2 ranged between 425 µatm and 475 µatm with a drop to 375 µatm in mid-August; these values are larger than the mean summer atmospheric value in the Arctic (~340–345 µatm). The photosynthetic active radiation (PAR) record demonstrated near-zero values until mid-June when the snow and sea ice began to melt and reached its maximum value in July, but no correlation between PAR and values of pCO_2 has been found (Semiletov et al., 2007). The source of those high values may be high rates of bacterial respiration (Rich et al., 1997) and may indicate a rapid turnover of sub-ice DOM which is closely connected with high sea-ice algal production (e.g. Gosselin et al., 1997). Import of the upper halocline water from the Chukchi Sea, where values of pCO_2 range as high as 400–600 µatm (Pipko et al., 2002), may also play a role in establishing high pCO_2 values beneath the perennial sea-ice. Another explanation for such a phenomenon involves the Lena River plume. Surface water from the Laptev Sea shelf, rich in runoff, dissolved CO_2, and DOM, follows the Gakkel Ridge towards Fram Strait (Anderson et al., 1998). This could explain the high concentration of DOM measured over the Amerasian shelf and Arctic Basin (Wheeler et al., 1996; Opsahl et al., 1999). Surface water concentrations of humic substances were ten times higher in the 87–89° N band than in 70–85° N band, associated with salinities of 31 instead of 34, presumably reflecting a clear signal of terrestrial carbon near the North Pole from the Lena plume as part of the Transpolar Drift (Sobek and Gustafsson, 2004). Hence the influence of the Lena River propagates throughout the interior Arctic basins.

The carbonate system parameters from all seasons show that the river is supersaturated in CO_2 compared to the atmosphere, up to 1.5–2 fold in summer, and 4–5 fold in winter. This results in a narrow zone of CO_2 supersaturation in the shallow-mid shelf sea, although offshore waters are generally undersaturated. Macro-synoptical conditions determine the distribution of pCO_2 in the southeastern Laptev Sea; either (a) the anti-cyclonic pattern dominates over the Arctic Basin (Proshutinsky and Johnson, 1997; Semiletov et al., 2000) and the transport of river runoff is northward causing a northward extension of the surface layer supersaturated in CO_2, as shown for September of 2008 by Pipko et al. (2011) or (b) the cyclonic pattern dominates and the northward transport of river water decreases compared to the anticyclonic situation, resulting in a decrease of the supersaturated surface layer north off the Lena Delta and eastward propagation of the Siberian Coastal current enriched by CO_2. Note, that the highest regional CO_2 supersaturation (up to 15 times) induced by oxidation of eroded carbon was found in winter in the nearshore zone adjacent to the Lena delta (Semiletov et al., 2004a, 2007).

BGD
8, 2093–2143, 2011

4.4 Dissolved methane (CH_4) in the Lena River – Laptev Sea system

The first dissolved CH_4 measurements were taken in the Lena River delta channels in fall of 1994 (Semiletov et al., 1996a, b). In the Lena River delta the concentration of dissolved CH_4 was usually below detection limit (which was ~15 nM at that time) during summertime: the highest concentrations (50–70 nM) were found in the Neelovsky Gulf in the southeastern part of the delta. However, during the ice-covered season, the concentration of CH_4 varied from trace up to 100 nM in the Bykovsky Channel and Neelovsky Gulf and in the Olenek Channel (Semiletov, 1999a). This indicates that wintertime high concentrations of CH_4 may be somehow related to degradation of permafrost in the Lena basin especially in the fault zones and drainage of thaw lakes enriched in dissolved CH_4 (Semiletov et al., 1996a, 2004b; Shakhova et al., 2005, 2010a, b). Thaw lakes with dissolved CH_4 concentrations ranging over two orders of magnitude from $\sim 10^{-2}$–10^{0} µM in the high Arctic (Lena Delta/Tiksi area) to ~10–10^{1} µM in the Subarctic (Kolyma Lowland/Cherskiy area), which are connected to the Siberian permafrost rivers by numerous channels and through taliks, would be an additional source of riverine CH_4, dissolved CO_2, and DOC (Shakhova et al., 2005; Semiletov et al., 1996a, b, 2004b). That agrees well with increasing dissolved CH_4 concentrations in the Lena River compared with the Ob which is located mostly in a non-permafrost zone (Shakhova et al., 2007a). In an early phase of these investigations, based on the data obtained in the Laptev and East Siberian Seas in cruises of 2003 and 2004, Shakhova and Semiletov (2007) found a significant correlation between integrated CH_4 storage and integrated salinity values ($r = 0.61$) or integrated values of TCO_2 ($r = 0.62$); both these features characterize marine water as compared to the fresh water flowing onto the shelf from rivers and streams. That suggests that riverine dissolved CH_4 export can only play a minor role for the dissolved CH_4 content of shallow shelf water.

In contrast, anomalously high concentrations of dissolved CH_4 (up to 5 µM) and an episodically (non-gradually) increasing atmospheric mixing ratio of (up to 8.2 ppm) were measured in some areas of the ESAS (Semiletov, 1999a; Shakhova et al.,

BGD
8, 2093–2143, 2011

2007b, 2010a, b). Results of high-performance studies made in the Lena Delta Channels in early September 2006 (Shakhova et al., 2010a, b) and along the Lena River from Yakutsk to the Laptev Sea in the late August–September of 2008 are shown in Fig. 11. The dissolved CH_4 spot (up to 125 nM) was detected only at the beginning of the Olenekskaya Channel (Fig. 3), where ice-complex bank erosion provides a huge amount of eroded OM, forming the anaerobic bottom environment which is conducive to early diagenetic CH_4 production. The Olenekskaya Channel is also underlain by a fault zone which may allow the formation of through taliks, disturbing the permafrost-associated hydrates (Collett and Dallimore, 2000; Shakhova and Semiletov, 2007; Shakhova et al., 2010a, b). However, in the Bykovsky Channel (the deepest among other Lena Delta channels) we detected a drastic decrease in dissolved CH_4 concentration downstream. This picture is further consistent with low CH_4 atmospheric emission (~10 mg m^{-2} d^{-1}) found recently in the Lena Delta (Ulrich et al., 2009) and our high-precision (Shakhova et al., 2010a, b) air CH_4 measurements made in 2006 along the Lena River channels which demonstrated relatively low values (~1.90 ppm) vs. moderate (1.95–2.10 ppm) and high (>2.10 ppm) found over the ESAS. Taken together, riverine export of CH_4 only plays a minor role in the CH_4 budget of ESAS coastal waters.

5 Conclusions

The Lena River integrates biogeochemical signals from its vast drainage basin and its signal reaches far out over the Arctic Ocean. The annual Lena River discharge of POC may be equal to 0.38 Tg (moderate to high estimate). If we instead accept Lisytsin's (1994) statement concerning the precipitation of 85–95% of total PM (and POC) on the marginal "filter", then only about 0.03–0.04 Tg of POC reaches the Laptev Sea from the Lena River. The Lena's POC export would then be two orders of magnitude less than the annual input of eroded terrestrial carbon onto the ESAS, which is about 4 Tg.

BGD
8, 2093–2143, 2011

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Transformation of riverine organic carbon into mineral carbon, and mineral carbon into the organic form in the Lena River watershed, can be considered a quasi-equilibrated processes. Significant inter-annual variability in mean values of TIC, TOC, and their sum (TC) has been found. This variability is determined by changes in land hydrology which cause differences in the Lena discharge because a negative correlation may be found between TC in September and mean discharge in August (a time shift of about one month is required for water to travel from Yakutsk to the Laptev Sea). Increasing the Lena River discharge causes opposite effects on dissolved organic and inorganic carbon: TOC concentration increases, while TCO_2 concentration decreases. Total carbon entering the sea with the Lena discharge is estimated to be almost 10 Tg C y^{-1}.

The Lena River is characterized by relatively high concentrations of primary greenhouse gases: CO_2 and dissolved CH_4. During all seasons the river is supersaturated in CO_2 compared to the atmosphere: up to 1.5–2 fold in summer, and 4–5 fold in winter. This results in a narrow zone of significant CO_2 supersaturation in the adjacent coastal sea. Spots of dissolved CH_4 in the Lena delta channels may reach 100 nM, but the CH_4 concentration decreases to 5–20 nM towards the sea, which suggests only a minor role of riverborne export of CH_4 for the ESAS CH_4 budget in coastal waters. Instead, the seabed appears to be the source that provides most of the CH_4 to the Arctic Ocean.

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Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀︎ ▶︎
◀︎ ▶︎
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 1. Major components of the carbon cycling and silica sampled between Yakutsk, the Lena Delta and Tiksi Bay (late August–early September 1995).

N_{CT}	pH_{25}	TCO_2, mM	TOC, mM	Si, µM	pCO_2, µatm	TCO_2 + TOC, mM
Yakutsk – Stolb Is.						
1	7.94	0.92	0.46	91.0	479	1.38
2	7.90	0.75	0.59	89.9	428	1.34
3	7.79	0.78	0.45	85.9	569	1.23
4	7.78	0.64	0.57	90.3	486	1.21
5	7.67	0.66	0.75	88.2	577	1.41
6	7.57	0.66	0.89	88.4	727	1.55
7	7.66	0.66	0.93	83.4	613	1.59
8	7.68	0.65	0.69	82.4	575	1.34
9	7.67	0.63	0.63	81.7	568	1.26
10	7.78	0.82	0.75	85.7	597	1.57
11	7.81	0.75	0.63	81.6	499	1.38
12	7.84	0.84	0.58	80.8	532	1.42
13	7.90	1.00	0.47	78.8	558	1.47
14	7.94	1.07	0.67	80.8	558	1.74
15	7.96	0.99	0.52	77.0	474	1.51
16	7.95	1.01	0.48	77.0	494	1.49
17	7.95	1.02	0.43	85.8	498	1.45
18	8.01	0.95	0.56	74.6	380	1.51
19	7.95	1.06	0.58	77.0	487	1.64
20	7.86	0.92	0.43		522	1.35
21	7.80	0.93	0.52	72.4	611	1.45
22	7.81	0.93	0.39	72.3	593	1.32
Mean	7.83	0.85	0.59	82.1	538	1.44
The Lena Delta – Tiksi Bay						
23	7.83	0.90	0.40	72.1	540	1.30
24	7.86	0.84	0.53	71.4	470	1.37
25	7.85	1.03		71.1	589	
26	7.86	0.99	0.38	63.9	544	1.37
27	7.87	0.99	0.38		520	1.37
28	7.75	1.01	0.38	52.5	717	1.39
29	7.85	0.95	0.39	52.5	534	1.34
30	7.82	0.93	0.39	52.5	551	1.32
31	7.87	0.98	0.40		526	1.38
32	7.78	0.94	0.40	52.5	609	1.34
33	7.82	1.04	0.42	63.9	608	1.46
34	7.76	1.14	0.45	41.3	715	1.59
35	7.83	0.96	0.39	38.7	523	1.35
36	7.81	0.96	0.47	43.8	513	1.43
37	7.81	1.16	0.38	52.5	593	1.54
38	7.78	1.36	0.43	47.2	688	1.79
39	7.78	1.25	0.47	37.4	585	1.72
40	7.75	1.38	1.30	31.5	682	2.68
41	7.79	1.32		35.0	736	
Mean	7.81	1.06	0.47	51.8	592	1.51

BGD
8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

Table 2. Mean concentrations of TOC, TCO_2, TC obtained along the Lena River stream (from Yakutsk to the Laptev Sea), and the Lena River discharge (W) in August of different years.

Time	TCO_2, mM	TOC, mM	TC, mM	W, km^3
September 1995	0.95	0.53	1.42	50.35
September 1998	0.65	0.58	1.24	56.51
September 1991 (SPASIBA-2)	0.60	0.60	1.20	62.94

BGD
8, 2093–2143, 2011
Biogeochemical signature of the Lena River
I. P. Semiletov et al.

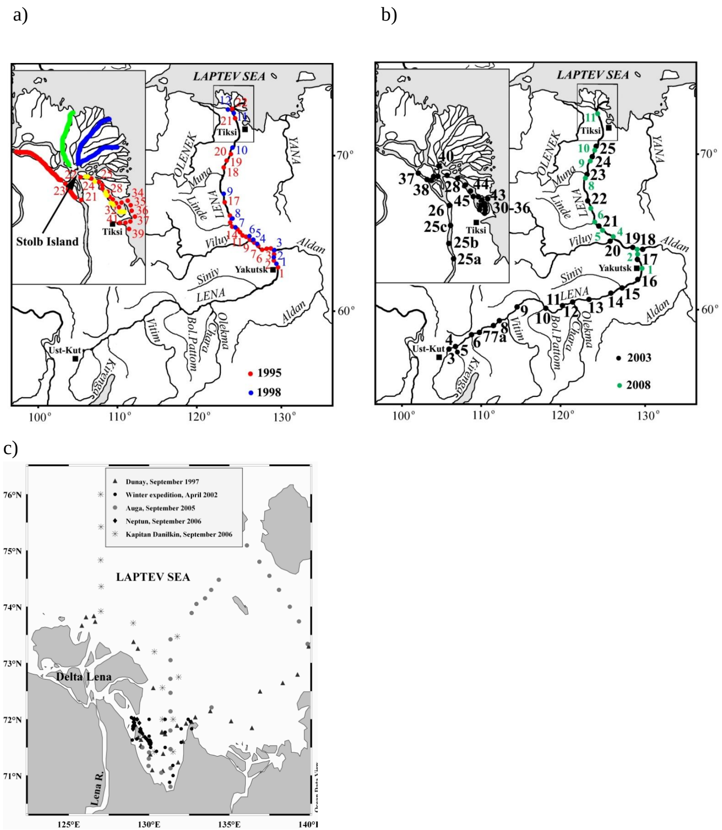

Fig. 1. Map of the study area location: **(a)** the Lena River stations, late August–early September 1995 and September 1998; **(b)** Lena River stations, September 2003 and 2008; **(c)** the Laptev Sea stations, September 1997, 2005, 2006 and April 2002. Location of major channels is marked by yellow (Bykovsky Channel), blue (Malaya and Bol'shaya Trofimofskaya Channels), green (Tumatskaya Channel), and red (Olenekskaya Channel) colors.

BGD
8, 2093–2143, 2011

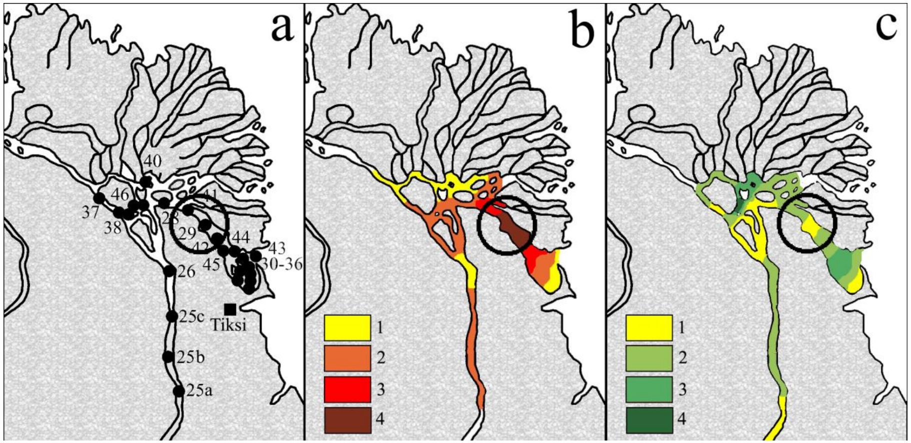

Fig. 2. (a) Distribution of sampling sites in the Lena lower stream-delta channels in the late July–early August 2003; **(b)** PM distribution in the surface layer, mg l^{-1}: (1) <10, (2) 10–20, (3) 20–30, (4) >30 and **(c)** POC distribution in the surface layer, mg l^{-1}: (1) <1, (2) 1–1.3, (3) 1.3–1.6, (4) >1.6.

BGD
8, 2093–2143, 2011

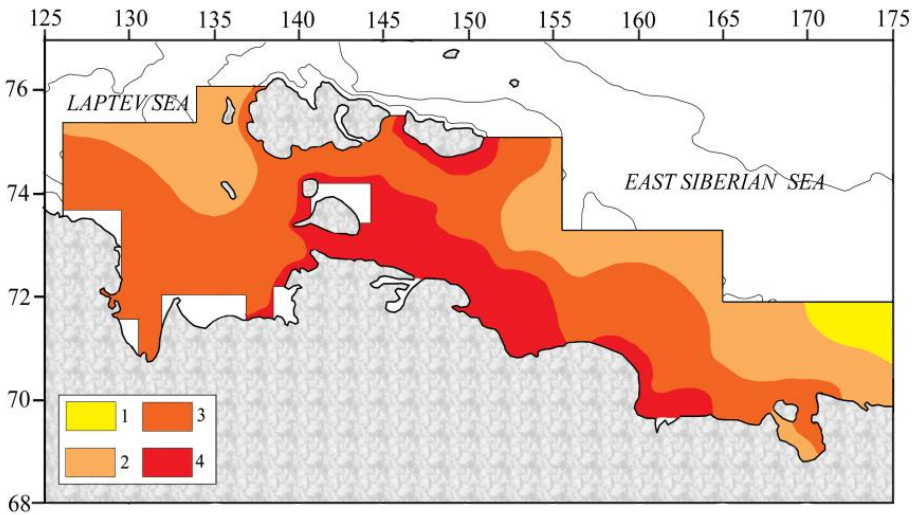

Fig. 3. CTOM (%) in the ESAS surface sediment: (1) <40%, (2) 40–69%, (3) 69–98%, (4) 98–100%.

BGD

8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◄I | ►I
◄ | ►
Back | Close
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

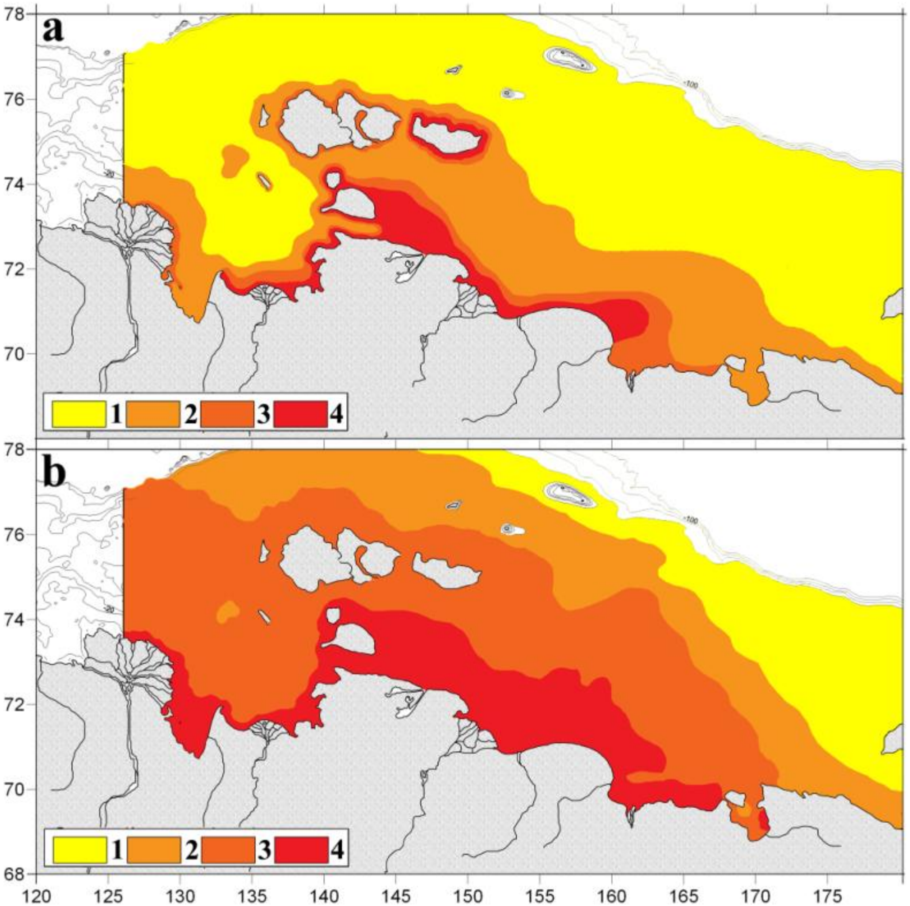

Fig. 4. Distribution in the ESAS surface sea water of: **(a)** particular materials (PM, $mg\,l^{-1}$): (1) <2, (2) 2–13, (3) 13–24, (4) >24; **(b)** CTOM of POC (%) (1) <25, (2) 25–50, (3) 50–75, (4) >75.

BGD

8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀I ▶I
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

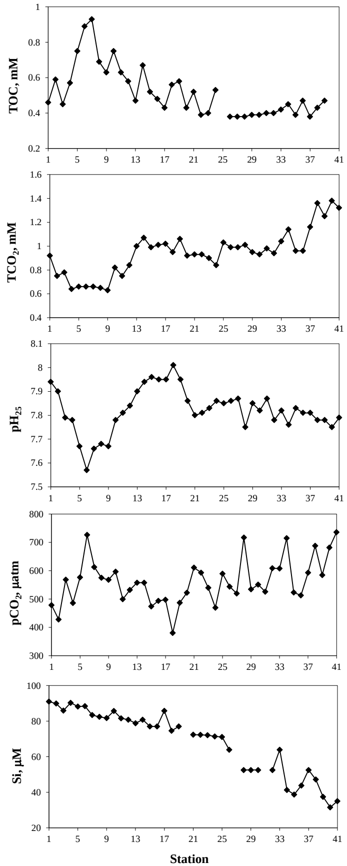

Fig. 5. Distribution of measured total organic carbon (TOC), total CO_2 (TCO_2), pH_{25}, silicates (Si) and calculated partial pressure of dissolved CO_2 (pCO_2) along the Lena River from Yakutsk to Tiksi: stations 1–22 (from Yakutsk downstream to the delta, Stolb Island); stations 23–38 (from Stolb Island to the Laptev Sea), late August–early September 1995.

BGD
8, 2093–2143, 2011

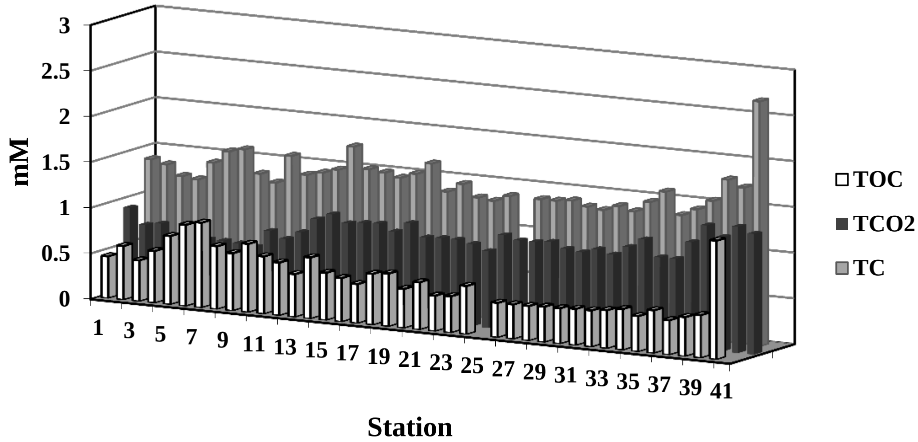

Fig. 6. Distribution of measured total organic carbon (TOC, mM), total inorganic carbon (TCO_2, mM) and total carbon (TC, mM) along the Lena River stream from Yakutsk to Tiksi (late August–early September 1995).

BGD

8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

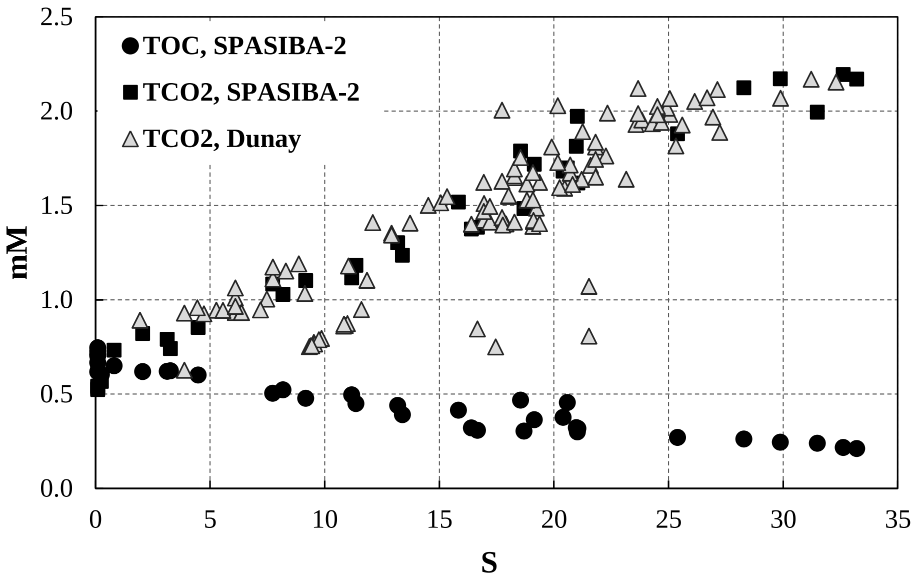

Fig. 7. The mean values of total organic carbon (TOC) and total inorganic carbon (TCO_2) vs. S measured in September 1991 (adopted by Cauwet and Sidorov, 1996) and in September 1997 onboard HV Dunay.

BGD

8, 2093–2143, 2011

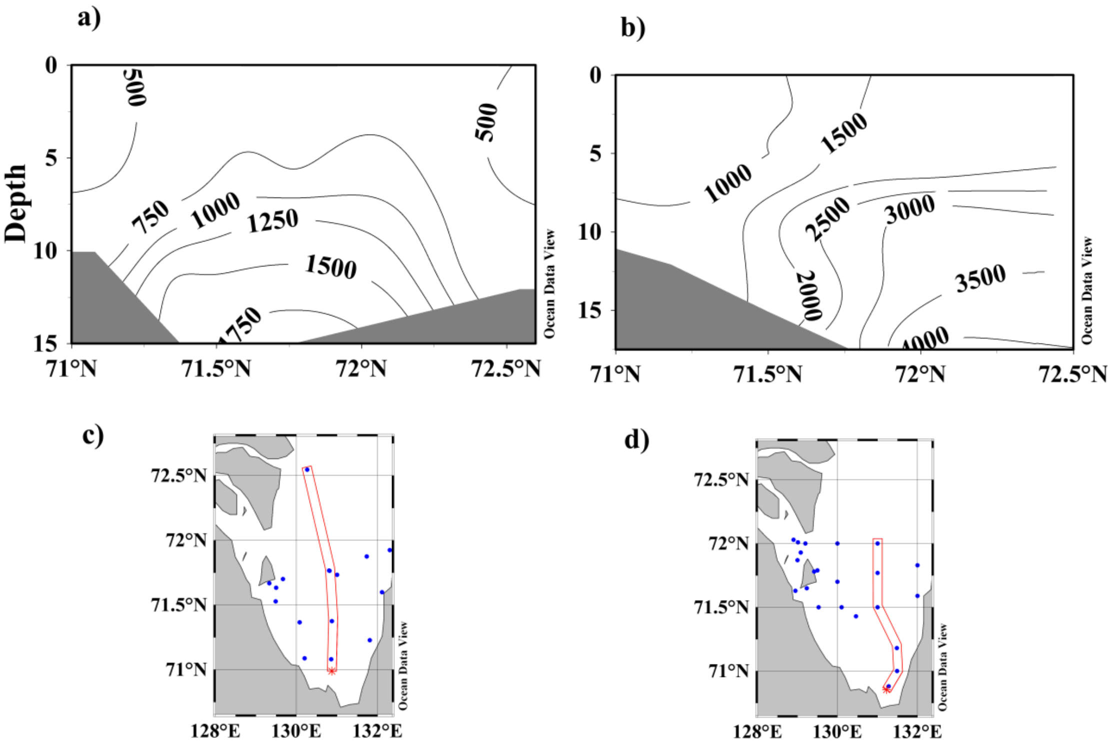

Fig. 8. Meridian vertical pCO_2 (μatm) profile across the Buor-Khaya Gulf of the Laptev Sea: **(a)** summertime distribution (September 1997); **(b)** wintertime distribution (April 2002) and transects position in **(c)** 1997, **(d)** 2002.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

BGD

8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

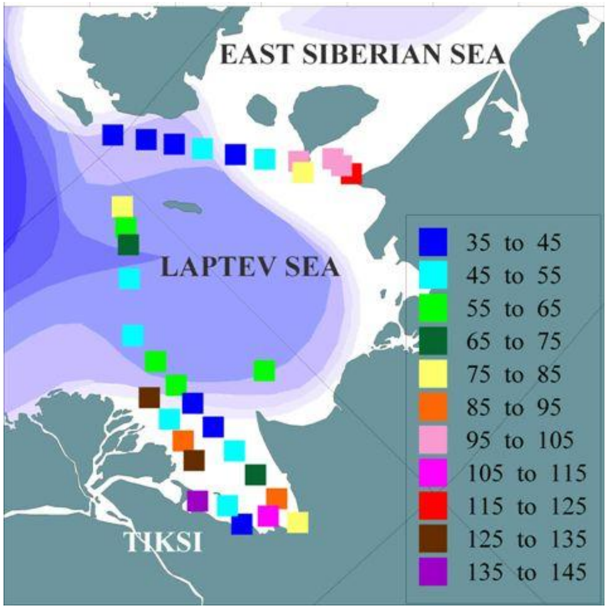

Fig. 9. Distribution of ΔpCO_2 (µatm) between the surface water and atmosphere in the Laptev Sea, September 2005.

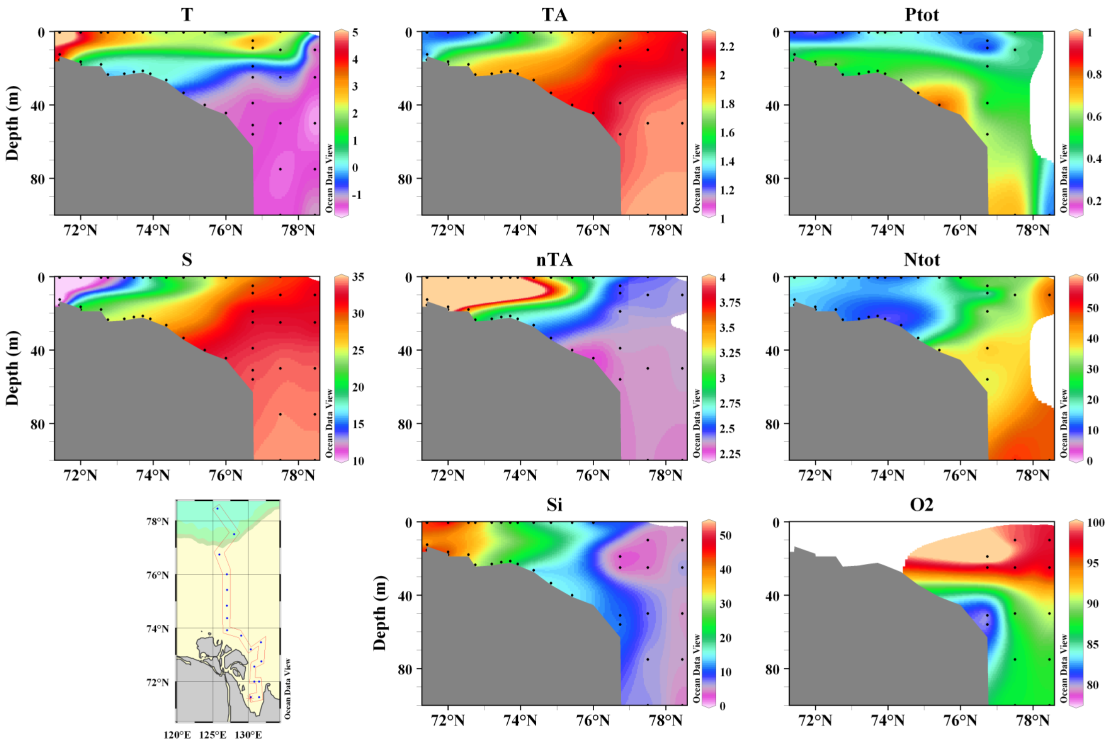

Fig. 10. Vertical distribution of temperature (T, °C), salinity (S), total alkalinity (TA, mmol kg^{-1}), normalized total alkalinity (nTA, mmol kg^{-1}), silicates (Si, µM), total dissolved phosphorus (P_{tot}, µM), total dissolved nitrogen (N_{tot}, µM) and oxygen saturation (O_2, %) within the south-north transect across the Laptev Sea, September 2006.

BGD
8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.

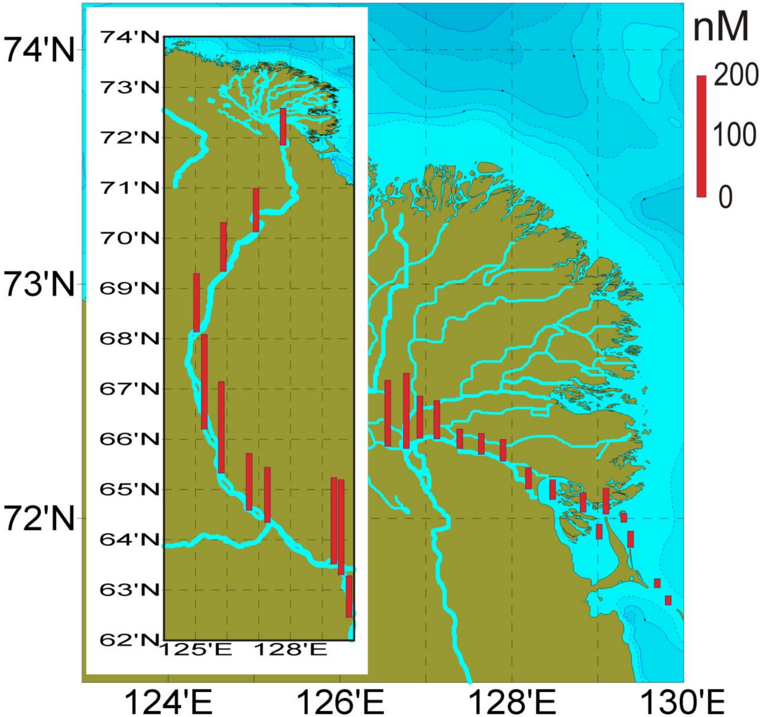

Fig. 11. Distribution of dissolved CH_4 (nM) in the Lena River, September 2008.

BGD

8, 2093–2143, 2011

Biogeochemical signature of the Lena River

I. P. Semiletov et al.