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Interannual variability of air-sea CO_2 fluxes and carbonate system parameters in the East Siberian Sea

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Abstract

Over the past couple of decades it has become apparent that air-land-sea interactions in the Arctic have a substantial impact on the composition of the overlying atmosphere (ACIA, 2004). The Arctic Ocean is small (only ~4% of the total World Ocean), but it is surrounded by offshore and onshore permafrost which thaws at increasing rates under warming conditions releasing carbon dioxide (CO_2) into the water and atmosphere. This work summarizes data collected from three expeditions in the coastal-shelf zone of the East Siberian Sea (ESS) in September 2003, 2004 and late August–September 2008. It is proposed that the western part of the ESS represents a river- and coastal erosion-dominated ocean margin that is a source for atmospheric CO_2. It receives substantial river discharge that also adds organic matter, both dissolved and particulate. This in combination with significant input of organic matter from coastal erosion makes this region being of dominantly heterotrophic character. The eastern part of the ESS is a Pacific water-dominated autotrophic area. It's a high-productive zone, which acts as a sink for atmospheric CO_2. The year to year dynamics of partial pressure of CO_2 in the surface water as well as the sea-air flux of CO_2 varied substantially. In some years the ESS shelf can be mainly heterotrophic and serve as strong source of CO_2 (year 2004). Another year significant part of the ESS, where gross primary production exceeds community respiration, acts as a sink for the atmospheric CO_2 and the net CO_2 flux into the atmosphere is weak (year 2008). High variability of carbon system parameters observed in the ESS shelf is determined by many factors such as riverine runoff, advection of waters from adjacent seas, coastal erosion, primary production/respiration etc. The dynamics of the CO_2 sea-air exchange is determined by ocean processes but also by atmospheric circulation which hence has a significant impact on the CO_2 sea-air exchange. In this contribution the sea-air CO_2 fluxes were evaluated in the ESS based on measured carbonate system (CS) parameters data and annual sea-to-air CO_2 fluxes were estimated. It was shown that the total ESS shelf is a net source of CO_2 for the atmosphere at a range from 0.5×10^{12} to 3.3×10^{12} g C.

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1 Introduction

The Arctic has undergone dramatic change during the past decades. Climate change has led to remarkable environmental alterations in the Arctic Ocean and its surrounding permafrost (ACIA, 2004; Macdonald et al., 2008; Savelieva et al., 2000). Climate changes include atmospheric sea-level pressure, wind fields, sea-ice drift, ice cover, length of melt season, variation in precipitation patterns and in land and marine hydrology. It is likely that these primary changes impact the carbon cycle and the biological systems (McDonald et al., 2008; Vetrov and Romankevich, 2004). The coastal ocean plays a disproportionately important role in the ocean's biogeochemical cycle despite its small areal fraction as it acts as a link between terrestrial, atmospheric and oceanic carbon reservoirs. Input, production, degradation and export of organic matter in the coastal ocean are several times higher than in the open ocean (Wollast, 1998). Consequently, it can be expected that the CO_2 exchange between the atmosphere and coastal environments is more intense than in the open ocean and thus is significant for the global carbon budget despite their relative small surface area (Borges et al., 2006). This is especially the situation in the Arctic Ocean where terrestrial and coastal permafrost is a huge reservoir of organic carbon that is bio-available (Stein and Macdonald, 2004) and already is involved in the modern biogeochemical cycle (Guo et al., 2004; Semiletov et al., 2007; van Dongen et al., 2008; Anderson et al., 2009; Vonk et al., 2010).

The issue whether continental shelves are a sink or a source of atmospheric CO_2 i.e. whether continental shelves are net autotrophic or net heterotrophic is far from certain (Cai et al., 2003) even for low and temperate latitudes. The Arctic Ocean's role in determining regional CO_2 balance has largely been ignored, because of its small size (only ~4% of the world ocean area) and because its continuous sea-ice cover is considered to impede gaseous exchange with the atmosphere so efficiently that no global climate models include CO_2 exchange through sea ice. However, the land-shelf-air interaction in the Arctic has a substantial impact on the composition of the overlying atmosphere; as the permafrost thaws, a significant amount of old terrestrial carbon becomes available for biogeochemical cycling and oxidation to CO_2 (Semiletov et al., 2007; Semiletov, 1999ab). Little CO_2 data are available over the high latitude continental shelves, especially for the ESS where the highest rates of coastal erosion were detected (Grigoriev et al., 2006).

The ESS is the shallowest marginal sea of the Arctic Ocean. Its average depth is about 54 m, the area is about 913×10^3 km^2 and the volume is about 49×10^3 km^3 (Gorshkov, 1980). It is, or at least has been, the most inaccessible among other Siberian arctic seas. This has primarily been related to comparatively heavy ice conditions, which often prevented navigation in this region even throughout the summer season. Generally, by the end of summer when the open sea area is maximum the drifting ice covers about 60–70% of the area forming the so-called Ayon ice massif in the central ESS (Kulakov et al., 2003). The hydrological and hydrochemical conditions in the ESS are dominated by Siberian river discharge, ice-related processes (ice formation and melting as well as brine rejection in coastal polynyas), vertical mixing, and exchange with the deep central Arctic Ocean basin and adjacent seas. The ESS can be characterized as an "interior shelf", which is highly influenced by exchanges with other shelves (Carmack et al., 2006).

The Arctic Ocean receives by far the most river discharge of the world's oceans (Carmack et al., 2006), but the direct river discharge into the ESS by the Kolyma and Indigirka rivers is small and averages only 0.3% of its volume annually. Significant part of the ESS freshwater budget is added by Lena River water, which penetrates in the ESS through the Dm. Laptev Strait and straits of Novosibirsky Islands. The Siberian Coastal Current is forced by winds and fresh water from rivers and sea ice melt, has its roots in the Lena River runoff, and flows eastward along the ESS coast (Nikiforov and Shpaikher, 1980; Semiletov et al., 2000; Weingartner et al., 1999).The volume of the Lena River discharge is one order of magnitude higher than that of the Kolyma. Due to the extreme climate the Lena, Indigirka and Kolyma rivers are characterized by extensive summer floods and a low winter discharge (Fig. 1). About 75–95% of

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the discharge occurs during warm season (http://rims.unh.edu). The heating effect of the Lena River plume in the ESS is illustrated by the warming of the shallow ESS sediments of up to 3 °C (Shakhova and Semiletov, 2007).

The shallow ESS shelf has the largest gradients in all oceanographic parameters observed for the entire Arctic Ocean (Semiletov et al., 2005). The highest rates of coastal erosion with its consequences for offshore flux of eroded material occurs here (Dudarev et al., 2003; Stein and Macdonald, 2004; Grigoriev et al., 2006).

The ESS has a unique geographic location as it is situated on the eastern Siberian Arctic shelf within the zero vorticity contour separating two predominant large-scale centers of atmospheric circulation over the Arctic Ocean (Nikiforov and Shpaikher, 1980; Proshutinsky and Johnson, 1993; Johnson and Polyakov, 2001). During anti-cyclonic circulation phases the high sea level pressure (SLP) centered in the western Arctic (the Siberian High) is well developed and the Icelandic Low is suppressed. During cyclonic phases the SLP in the western Arctic is weaker and the Icelandic Low is stronger, extending farther into the Barents and Kara Seas (Johnson and Polyakov, 2001). This makes the oceanographic state of the ESS sensitive to the dominated type of atmospheric circulation. The response of the ESS to changes in atmospheric pressure consists in the redistribution of surface waters (Nikiforov and Shpaiher, 1980). Dmitrenko et al. (2005) found that there was a good correlation between a summer vorticity index and sea surface salinity patterns over the Laptev and East Siberian Seas.

The wind waves are comparatively weakly developed in the ESS due to the ice cover extent and shallow water. With ice retreating northward during the period from July to September, the frequency of strong waves increase and reach its maximum in September. At this time the wave heights can be up to 5 m (our observations) that might mix the water column from top to bottom in the shallow areas (depth <30 m) causing resuspension of fine bottom material. With increasing frequency of Arctic cyclones and strong storm events (ACIA, 2004; Serreze et al., 2000) together with less ice coverage this mixing might be a factor for additional warming of surface sediment causing further thawing of permafrost leading to bottom erosion.

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The ESS hydrography has been fairly well studied, but dynamics of the carbonate system has been poorly investigated except for our previous studies (Olsson and Anderson, 1997; Pipko et al., 2005, 2008ab, 2009; Semiletov, 1999ab; Semiletov et al., 2007; Semiletov and Pipko, 2007; Anderson et al., 2009).

In this study we present CS parameters data from the ESS surface water based on three year surveys (September of 2003, 2004, and late August-September 2008). The spatial and interannual variability of CS characteristics and metabolic status in the ESS are discussed in relation to highly variable meteorological regimes, river discharge, and intensity of coastal erosion. Based on the sea-air CO_2 difference and measured wind speed, we compute the sea-air CO_2 flux over the ESS, and its interannual variability. To date, this is the first estimation of net CO_2 flux based on multi-years direct CS parameters measurements.

2 Materials and methods

Hydrographic observations and sampling were carried out in the ESS during hydrological summer in September 2003, 2004 and August–September 2008 (Table 1, Fig. 2). pH was determined potentiometrically and reported on the total hydrogen ion concentration scale (DOE, 1994). The precision of the pH measurement was about ± 0.004 pH units. NBS commercial standard buffers were used to check the Nernst slope of the combination electrode. Seawater samples were collected in Niskin bottles mounted on the CTD rosette and then transferred into smaller bottles for chemical analysis. In September 2003 and 2004 samples for total alkalinity (A_T) were determined as proposed in DOE (1994). The A_T samples were poisoned with a mercuric chloride solution at the time of sampling. Samples were kept in the dark and were analyzed in the lab within one month using an indicator titration method where 25 ml of seawater was titrated with 0.02 M HCl in an open cell according to Bruevich (1944). In 2000 the Carbon Dioxide in the Ocean working group of the North Pacific Marine Science Organization (PICES) performed an intercalibration of A_T in seawater using

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certified reference materials (CRM). The results of the intercalibration showed that the alkalinity values obtained by the Bruevich method are in agreement with the standard within $\pm 1\,\mu mol\,kg^{-1}$ when state of the art analytical practice is applied (Pavlova et al., 2008).

In August–September 2008 total alkalinity was determined after pH from the same bottle on board of "Yakob Smirnitskiy", using an open cell potentiometric titration method. HCl of 0.05 M concentration was used and the endpoint was determination by a Gran function (Haraldsson et al., 1997). The obtained concentrations were calibrated against CRMs supplied by A. Dickson, Scripps Institution of Oceanography. The precision of both titration methods was similar at about 0.1%.

In the 2003 and 2004 cruises atmospheric CO_2 concentration was measured using the non-dispersive infrared CO_2 analyzer LI-820 with accuracy better than 3% (www.licor.com), while in the 2008 cruise the high precision open-path LiCor-7500 was used. The seawater partial pressure of carbon dioxide (pCO_2) was computed from pH-A_T using CO2SYS (Lewis and Wallace, 1998).

During 2003–2004 cruises a Seabird Profiler SBE19plus (www.seabird.com) was used for measurements of conductivity, temperature, photosynthetic active radiation (PAR) (by LI-193SA Spherical Quantum Sensor), turbidity (by OBS-3 Sensor) and fluorescence (by WetStar fluorimeter, Ex = 370×10^{-9} m, Em = 460×10^{-9} m) that characterized the distribution of colored dissolved organic matter (CDOM) at 0.20 m intervals in the vertical at the oceanographic stations. In August–September 2008 the Seabird Profiler SBE19plus measured these parameters along the ship route each minute in the 300 l barrel with flowing sea water (pumped from 4 m depth with a rate of about 40–50 l per min) and a Seabird Profiler SBE911plus was used to collect data (conductivity and temperature) in the water column at each oceanographic station. Dissolved oxygen (O_2) concentrations were obtained using Winkler titration system, giving a precision of $\sim 3\,\mu mol\,kg^{-1}$ for 2003–2004 data and $\sim 1\,\mu mol\,kg^{-1}$ for 2008 data. These values were then converted to a percent saturation, following Weiss (1970).

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The equation published by Wanninkhof and McGillis (1999) was used to calculate the CO_2 flux (F_{CO_2}).

$$F_{CO_2} = K_0 \times k \times (pCO_2{}^{sw} - pCO_2^{air}), \quad (1)$$

where K_0 is the solubility of CO_2 at the in situ temperature (mol m^{-3} atm^{-1}), k is the gas transfer velocity (cm h^{-1}), u is the wind speed (m s^{-1}), and Sc is the Schmidt number for CO_2 defined by Wanninkhof (1992). The wind speeds used in the calculation of transfer velocity were daily averaged values measured on board during each cruise.

3 Results

The marine carbon cycle is largely determined by the forcing factors like wind, sea ice and runoff, and these conditions are firstly described.

3.1 Meteorological situation

The NCEP sea level pressure data were employed to describe the atmospheric circulation over Arctic Ocean (www.esrl.noaa.gov). The SLP fields, averaged over summer season (July–September) for each year, are shown in Fig. 3 and have substantial interannual variability. During the summer season of 2003 cyclonic atmospheric circulation dominated over the central Arctic Ocean. SLP down to 1005 mbar extended into the Laptev and the East Siberian Seas. In 2004 the summer low pressure north the ESS was weaker while an anticyclone, located above the Canadian Arctic Archipelago, had formed. In contrast to the situation in 2003–2004 during warm season of 2008 anticyclone dominated over the Canada Basin of the central Arctic Ocean and a low pressure was present over Siberia.

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3.2 Ice conditions

Our investigations were carried out in the late August-September period of maximal seasonal sea ice retreat. During all cruises the ice edge was well north of its 1979–2000 median September position and well off the coast of Siberia. The second-lowest satellite record sea ice extent occurred in 2008 (http://nsidc.org/news/press/). Figure 4 illustrates sea ice extent in the ESS during the period of the three expeditions (ice charts were obtained from www.aari.nw.ru). In September 2008 the ice free area was about 90% of the ESS area; in September 2003 about 60% and in September 2004 it was about 40%.

3.3 Hydrography

As stated earlier by Proshutinsky and Johnson (1993) the circulation in the ESS is driven by dominating winds, which can be deduced from the pressure field shown in Fig. 3. Dmitrenko et al. (2005) also note that at the average shelf depth of about 20–25 m the wind-forced flow is essentially controlled by wind stress and bottom friction, and the Coriolis force becomes insignificant and the surface current aligns almost completely with the wind direction. The spatial distribution of sea surface salinity and temperature obtained in 2003, 2004 and 2008 is shown in Fig. 5. In Fig. 6 sections of density, expressed as sigma (σ = 1000 x (density-1)), are shown for the along-shore transects.

The overall hydrological conditions in the coastal zone were mainly characterized by interaction of a warm and fresh waters from the Indigirka (152° E) and Kolyma (162° E) rivers with brackish waters from the Laptev Sea and relatively cold and saline water of Pacific origin from the Chukchi Sea (Fig. 5). Melting sea ice also contributes a significant fraction of the ESS freshwater budget. The sea surface salinity showed a general eastward increasing trend. The maximum and minimum salinity values varied between 8.49 (2004) and 30.39 (2008), but the latter was to the northeast at the shelf break. Surface temperature values ranged from –0.99 °C (2008) to 6.59 °C (2008). In

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general, temperature decreased eastward. Freshwater signal from the Kolyma and Indigirka rivers were detected by minimum salinity (~8.49, 2004) and high temperature (up to 6.17 °C, 2004). The isohaline 25 has been reported as a "conventional" boundary of river water propagation (Antonov, 1957). The maximum eastward spreading of river water was detected in September 2004 when the freshwater signal was found in the vicinity of the Long Strait. To the opposite, in the summer of 2008, freshened waters were shifted to the western part of the ESS where the sea surface temperature maxima and salinity minima in September for the years 2003, 2004 and 2008 were found. The lack of a low salinity band along the coast in 2008 showed that the Siberian Coastal Current was not well established this year, which was a result of changes in the atmospheric circulation pattern as shown in Fig. 3. The strength of the Siberian Coastal Current is also seen in the strong horizontal and vertical density gradients in the eastern part of the ESS in September 2003 and 2004 (Fig. 6). On the contrary sharp horizontal gradients were observed in the western part in late August-September 2008. In September 2003 and 2004 the water column in the western ESS near Dm. Laptev Strait was found to be almost homogenous, whereas in 2008 density increased with depth.

3.4 Distributions of surface water carbonate system parameters

The distributions of the CS parameters ($pH_{in\ situ}$, A_T, nA_T and pCO_2) in the ESS surface waters are shown in Figs. 7 and 8. Surface A_T values had a very wide concentration range (0.867–2.221 mmol kg^{-1}) with similar spatial gradients as surface salinity, i.e. the lowest values at stations where large amounts of river water have diluted A_T and salinity. There were also large variations in surface seawater $pH_{in\ situ}$ distribution on the ESS shelf (7.48–8.34 units). Maxima values of A_T and $pH_{in\ situ}$ were observed in the eastern part of the ESS and in September 2008 these values were the highest during the three surveys (Fig. 7). The lowest surface concentrations of A_T and pH were found over the ESS shelf in the summer of 2004. Variations in A_T, normalized to constant salinity (35), nA_T, were maximum in the summer of 2008 when these values ranged

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from 2.336 up to 3.641 mmol kg^{-1}. The observed features in the CS parameters largely reflect the hydrological characteristics as described above.

The pCO_2 data show strong and varying deviation from that of the atmosphere in the summer, both between the years and in space. In September 2003 the pCO_2 values in the surface layer varied from 252 to 521 µatm, in 2004 from 272 to 1033 µatm, and in 2008 – from 198 to 905 µatm (Fig. 8). The observations showed a clear and stable tendency in the spatial distribution of pCO_2 in the surface layer of the ESS, with low values to the east and with considerable fluctuations near estuaries and erosion shorelines. In the western part the surface water was oversaturated with CO_2 and in the east the pCO_2 values were significantly lower than atmospheric values (Fig. 8).

3.5 Air-sea fluxes of CO_2

The distributions of computed air–sea fluxes of CO_2 are illustrated in Fig. 9, and the statistics are listed in Table 2. Some general characteristics of the CO_2 flux distributions of the three cruises can be summarized as follows:

- In the shelf waters the CO_2 fluxes tended to be positive (CO_2 out-gassing) in the western part of the ESS and negative (CO_2 absorption) in the eastern part.
- In September 2003 minimum average magnitudes of CO_2 fluxes both positive and negative were calculated, within the range of 4.2 to −1.1 mmol m^{-2} day^{-1}.
- In September 2004, the CO_2 fluxes were positive except for a downward flux of −0.1 to −4.8 mmol m^{-2} day^{-1} restricted to the easternmost part of the ESS in the vicinity of Wrangel Island. The maximum CO_2 efflux was detected near the Kolyma River mouth (where also the highest rates of coastal erosion are known to occur) and it value reached 33.2 mmol m^{-2} day^{-1}.
- In late August–September 2008 values of CO_2 fluxes ranged from −5.0 to 19.4 mmol m^{-2} day^{-1} and the invasion area was the largest among the surveys (Fig. 9).

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4 Discussion

The dynamics of CS in the ESS is determined by interaction of different water masses and is further impacted by biological primary production (PP) and decay of organic matter, both by marine and terrestrial origin.

Ice cover for a major portion of the year prevents light from penetrating deep into the water column and thus limits PP in the arctic seas for several months. The ESS has a shorter season of PP mainly because of harsh ice conditions (ice-free period is about 60–75 days) (Vinogradov et al., 2000). Our surveys were carried out in late August-September when PP in the Arctic shelf seas is supposed to be high (Springer and McRoy, 2003; Alexander and Niebauer, 1981). Coastal erosion and river discharges provide a major source of suspended matter and nutrients. The Lena River is the second among the Siberian Rivers bringing 2.2×10^6, 2.2×10^4, 2.1×10^4 and 4.2×10^3 tons of nutrients in form SiO_2, NO_3^-, NH_4^+ and PO_4^{3-}, respectively, into the sea every year and limitation of PP by nutrients is negligible (Gordeev et al., 1996). But substantial input of terrestrial matter over the ESS shelf leads to low light conditions in the surface water even during summer season (Pipko et al., 2005, 2008a; Semiletov et al., 2007).

At present time no consensus on the productivity of the EES water due to the limited amount of data. The ESS is considered as an oligotrophic or a low productivity ecosystem (Sorokin and Sorokin, 1996; Vinogradov et al., 2000). Anderson et al. (2011) computed the ESS annual PP based on consumption of dissolved inorganic carbon and evaluated its magnitude to about 1 mol C m^{-2} or 6×10^{12} g C if integrated over half of the ESS area. Other estimations of the ESS annual PP are between $10–15\times10^{12}$ g C (Vinogradov et al., 2000; Vetrov and Romankevich, 2004; Berger and Primakov, 2007). Maximal value of total PP in the ESS was estimated to 45×10^{12} g C (Sakshaug, 2004), but the latter number is highly uncertain as it is calculated by extrapolation of data from the high-productive surrounding shelf seas.

The terrestrial organic matter is added to the sea by the river runoff and by coastal erosion (Grigoriev et al., 2006; Macdonald et al., 2008). The ESS has one of the

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shortest shoreline among the arctic seas (3500 km excluding islands and 5900 km total length) (Grigoriev and Rachold, 2003; Rachold, 2004) and the largest organic carbon input that originates from eroded coastal permafrost deposits (2.2×10^6 t C yr^{-1}), which are wide-spread in Northern Siberia especially along the ESS coast where they dominate (Grigoriev et al., 2006). Ice-complex and thermokarst deposits amount to 41% of total shoreline length, ice-poor Pleistocene -Holocene coasts to 27% and rocky and other types of non-icy coasts to 32% (Grigoriev et al., 2006). According to Grigoriev et al. (2006) the average retreat rate of coastlines consisting of ice-complex and lake-thermokarst deposits is estimated to about 3 m yr^{-1} along the ESS coast line. However, along some coastal sections, for example, the Svyatoi Nos Cape – the Kolyma River mouth alongshore transect, ~141° E–161° E, the rate of coastal erosion reaches 10–15 m yr^{-1}, which is the highest in the East Siberian region. It is approximately 33% of the total organic carbon flux to the Arctic Ocean through coastal erosion and the ESS is the only arctic sea where coastal total organic carbon input slightly exceeds riverine input (1.86×10^6 t C yr^{-1}) (Stein and Macdonald, 2004). The coastal erosion likely has increased lately due to permafrost thawing and the retreat of seasonal sea ice coverage which increases wave-based shoreline erosion (Serreze et al., 2000).

Models and geophysical data indicate that large areas of the Arctic shelves (including the ESS) are thought to be almost entirely underlain by subsea permafrost from the coastline down to a water depth of about 100 m, as a result of their exposure to the atmosphere during the Last Glacial Maximum (Romanovskii et al., 2005; Shakhova et al., 2010a). It has been found that the ESS sub-sea bottom permafrost erosion is quite high, ranging from 1 to 15 cm yr^{-1} (Grigoriev, 2006; Razumov, 2010). As a whole, the dynamics of sub-sea permafrost is still poorly known, due mainly to the lack of direct observations (Gavrilov, 2008; Rachold et al., 2007).

The pCO$_2$ values decrease from high over-saturation values in the west to under-saturation in the east of the study area, which is especially pronounced in 2008 (Fig. 8). This is accompanied by an increase in salinity and decrease in temperature (Fig. 5). The west-to-east pCO$_2$ decrease as a result of temperature reduction

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calculated using Lewis and Wallase program (Lewis and Wallase, 1998) amounted up to 0.0413–0.0430° C^{-1}, showing that the temperature distribution cannot explain all of the observed decrease in $p\mathrm{CO_2}$. In 2008 only about half of the $p\mathrm{CO_2}$ change can be explained by the temperature variability, while in 2003 and 2004 it can only explain one-fifth of the $p\mathrm{CO_2}$ change.

According to Semiletov et al. (2005) two hydrological regimes exist in the ESS one in the west and one in the east, identified by temperature and salinity as well as the ^{13}C isotope composition of the particulate material and bottom sediment. It was shown that position of the δ^{13}Corg isoline of −24.5‰ represents the boundary between the "typical terrestrial" δ^{13}Corg values (lighter than −24.5‰) in the western ESS and the "typical marine" values in the eastern ESS. The distribution of the carbon parameters in the surface water supports this conclusion, but demonstrated significant year-to-year variability in the location of the front. Some years, it deviate significantly from the long-term (climate) location of the sediment geochemical boundary because of changing atmospheric and water mass circulation patterns as discussed below.

4.1 Western East Siberian Sea

The shallow western part of the ESS is highly influenced by inflow of low salinity water from the Laptev Sea where the Lena River discharge dominates with additions from the Kolyma and Indigirka rivers. However, at least two freshwater sources, melted sea ice and in-situ precipitation are also significant components of the ESS freshwater budget, which complicates the analysis of runoff transport from salinity alone (Cooper et al., 2008). Several constituents have been used to separate and identify freshwater components in the Arctic from these specific sources (e.g. Anderson et al., 2004; Cooper at al., 2005; Fransson et al., 2009; Ekwurzel et al., 2001; Macdonald et al., 1995).

The river runoff has an excess of A_T, described by the distribution of total alkalinity normalized to S = 35 (nA_T), as well as of CDOM (Pugach et al., 2009, 2010) which mostly has a river origin. For example, in September 2003 and September 2004 coefficients of linear correlation of A_T-S values and CDOM-S values in surface water along

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the near-shore transect (position of transects is shown in Fig. 6) were 0.99 and 0.93 (A_T-S) and −0.96 and −0.86 (CDOM-S), respectively. Such strong correlation of A_T and CDOM values with salinity together with the offset at zero salinity suggests that rivers are strong sources of these components in the ice free ESS. The question concerning A_T fractionation during sea ice formation or melting is still under debate. It has been reported that sea ice formation or melting under natural conditions does not fractionate A_T (Anderson and Jones, 1985; Nedashkovsky et al., 2009). Rysgaard et al. (2007) suggested that the total alkalinity/dissolved inorganic carbon (A_T/C_T) ratio in sea ice changed compared to the A_T/C_T ratio of the surface water from which it was formed as a result of calcium carbonate ($CaCO_3$) precipitation when seawater freezes. Dieckmann et al. (2008) demonstrated direct evidence of $CaCO_3$ precipitation in sea ice, in the form of the mineral ikaite ($CaCO_3 \times 6H_2O$) in sea ice from the Southern Ocean. However, it's concentration is on average about 0.024 mmol l^{-1} which is a negligible exceed comparing with riverine value. Thus, we don't include the A_T fractionation by sea ice formation or melting in further consideration of the spatial distribution of nA_T in the ESS surface layer. Since the total alkalinity in precipitation is also negligible (Cooper et al., 2008) we regard nA_T as a tracer of river water over the ice-free Arctic shelf in September. Figures 8 and 10 illustrated that the western part of the ESS was strong influenced by river input of dissolved inorganic and organic carbon and its effect changes from year to year.

Runoff impacts the seawater composition not only in lowering salinity and increasing A_T and dissolved organic carbon (DOC), as the runoff also is characterized by low pH and high pCO$_2$ (Figs. 7 and 8). The high riverine pCO$_2$ is a result of decay of terrestrial organic matter in the drainage basins as well as in river's stream and estuaries (Guo et al., 2004; Van Dongen et al., 2008).

The ESS coast line is characterized by the occurrence of ice-rich deposits containing old organic carbon and they are most prevalent in the western part of the sea (Grigoriev et al., 2006). As mentioned above, the erosion rate of these deposits is among the highest in Arctic seas, and remineralization of the eroded organic matter adds to

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anomalies of high pCO_2. The fact that the organic matter buried in the permafrost is bio-available has been confirmed earlier (Semiletov, 1999ab; Guo et al., 2004; Van Dongen et al., 2008; Anderson et al., 2009; Vonk et al., 2010; Sánchez-Garcia et al., in press). In opposite, the major part of the dissolved organic matter that enters the sea with the river discharge was considered as not biodegradable (Dittmar and Kattner, 2003). However, recent findings suggest DOC to be variable in lability (Alling et al., 2010).

Thus, observed surface water oversaturation relative to atmospheric CO_2 level in the western part of the ESS is a result of inflow of warm and turbid, more acidic (in comparison to ocean) river waters with high CO_2 concentration, as well as intensive heterotrophic processes taking place, because of the large amount of allochthonous bio-available particulate organic matter added mainly by erosion.

Primary production rates in seawater are depending on the nutrient availability as well as the PAR, which penetrates to the water column. It is known, that attenuation of PAR in the open water column is caused by suspended particular matter (SPM) backscattering as well as adsorption by phytoplankton and CDOM. In regions with considerable river runoff absorption by CDOM exceeds that of phytoplankton absorption by ten times (Burenkov et al., 2001). In the western part of the area there was a sharper vertical extinction of PAR: the depths (H_5) where its intensity went down to 5% from the values in the surface layer comprised 3–16 m in the western area and went down to 30–33 m in the eastern area. This observation coincides well with the decrease in SPM and CDOM concentrations moving from the Dmitry Laptev Strait to the Long Strait (Fig. 10).

The SPM values (calculated from the turbidity data according to Shakhova and Semiletov, 2008) and CDOM concentrations in the surface waters of the western part of the ESS were one order of magnitude higher than in the eastern part, because of this area is highly influenced by river runoff and coastal erosion. Intensive wave and wind-mixing, typical for the shallow south-western part, leading to sediment resuspension might also add to the observed high SPM concentration (Semiletov et al., 2005;

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Dudarev et al., 2006). Furthermore resuspension of heterotrophic bacteria alongside SPM can increase the carbon dioxide concentration in the water column through the decomposition of organic matter (Amon and Benner, 1996). In addition to sediments that are resuspended off the seabed, SPM may also originate from a "benthic fluff" layer (Verspecht and Pattiaratchi, 2010) with its low-density organic material being available for degradation and remineralization. This thin (up to 1 m) near-bottom layer (also so-called "nepheloid") enriched by organic carbon was found in the ESS (Dudarev et al., 2009), and earlier in the Barents Sea (Romankevich et al., 2000). Concentration of organic carbon in this layer is one order magnitude higher relative to the overlying water (O. V. Dudarev, personal communication, 2010). During a wind event typical for the western part of the ESS during August–September, when bed shear stress and turbulence are high, the benthic fluff can become homogeneously distributed through the water column. Seabed erosion which has not been sufficiently studied yet may also be an additional source of SPM (Dudarev et al., 2008; Grigoriev, 2006).

Correlation of H_5 values against the SPM and CDOM values along the near-shore transect accomplished in 2004 were 0.71 and 0.91, respectively ($n = 18$). Moreover, the rate of the PAR extinction in layer H_5 showed a close relationship with those parameters – 0.98 and 0.93 (Fig. 11). At stations with similar turbidity but with higher CDOM, the decrease in PAR with depth is greater, which illustrates a significant role of fluorophores in changing PAR absorption. Thus, in the western part of the ESS a sharp attenuation of PAR was observed within the first several meters of water column that significantly reduced the depth of photic layer.

In September 2004 a linear correlation coefficients of $p\mathrm{CO_2}$ with CDOM and SPM at the alongshore section were 0.59 and 0.48, respectively. In September 2003 correlation coefficients of $p\mathrm{CO_2}$ with CDOM and SPM were 0.68 and 0.65.

Note, that values of PP measured in a survey of the ESS during early September 2000 (Semiletov et al., 2007) demonstrated a 5–8 times increase from the west to the east. Thus, near the Dm. Laptev Strait the magnitude of PP was 0.051 $\mathrm{g\,C\,m^{-2}\,day^{-1}}$ and in the eastern part of sea near Long Strait it was 0.299–0.406 $\mathrm{g\,C\,m^{-2}\,day^{-1}}$

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(unpublished data of I. Umbrumaynts, Institute of Global Climate and Ecology of Roshydromet and RAS). During the summer of 2000 the atmospheric circulation pattern was similar to that in the summer of 2008 (anticyclonic regime) and the eastern part was strongly affected by the Pacific-origin water inflow (Savel'eva et al., 2008). So, we can consider these values of PP and its spatial distribution as "typical" for years when high atmospheric pressure dominated over adjacent Arctic Ocean.

The homogenous density distribution in the western ESS (excluding the near-mouth zone) during Septembers 2003–2004 (Fig. 6) was an important factor of the high pCO_2 in the surface layer due to the more intensive CO_2 exchange with bottom layer. Note that gas transfer across the thermocline is a major rate-limited process (Matthews, 1999).

As a result of the factors mentioned above, waters in the western region of the ESS were oversaturated with respect to CO_2 compared to atmospheric values and characterized by net production of inorganic carbon and CO_2 release to the atmosphere (Fig. 9). Thus, the western part of the ESS represents a river- and thermo abrasion-dominated heterotrophic area.

4.2 Eastern East Siberian Sea

The eastern part of the ESS was strongly influenced by waters from the Chukchi Sea, whose biogeochemical conditions were determined by the inflow of transformed waters from the Pacific Ocean (clear, salty and high-productive, with high nutrient and inorganic carbon content). In the eastern part of the ESS the surface water pCO_2 values were lower than atmospheric pCO_2 (Fig. 8) as a result of high primary productivity, also supported by high pH and O_2 saturation values (Anderson et al., 2009; Pipko et al., 2008a). The water column had a double-layer structure with a well-defined pycnocline (Fig. 6). All the CS parameters had distinct different concentrations in the surface and bottom layers as is typical when primary production is active in the surface water and decay products from organic matter is added to the bottom water. Hence, seawater pCO_2 values in the surface water had low values (about 200–270 µatm). The

pCO_2 values in the bottom waters were about 5 times higher – up to 1200 µatm. Minimum values were observed in subsurface waters (10–20 m) at about 150–195 µatm. The O_2 saturation reached a maximum of 138% at these depths in Long Strait, a region much influenced by high nutrient and clear water from the Pacific Ocean. Such subsurface maximum of photosynthesis activity is typical for Chukchi Sea shelf where the upper layer is very clear and light penetrates to the lower layer with sufficient intensity to allow phytoplankton to grow rapidly at depth (Springer and McRoy, 1993). CO_2 fluxes in the eastern part of the ESS were downward and ranged from −0.12 to −5.03 mmol m^{-2} day^{-1} (Fig. 9). The intensive primary production with the resulting absorption of atmospheric CO_2 is an evidence of autotrophy in the ESS eastern region.

4.3 Interannual variability

Despite the fact that trends of spatial pCO_2 distribution in the surface water was the same during the summer of 2003, 2004 and 2008 (decrease from west to east), values of pCO_2 showed significant interannual variability (Fig. 8). The highest pCO_2 values were observed in September 2004 and reached 1033 µatm. The lowest values were obtained in September 2008 in the eastern part of the ESS. The position of the zero CO_2 flux curve also varied substantially between the September 2003, 2004 and 2008 (Fig. 9).

The largest year-to-year variability of CS parameters was observed in the central coastal zone of the ESS (Figs. 7, 8, 12). This area is the most dynamic one and is distinguished by interaction of waters with extreme characteristics – from river waters with close-to-zero salinity to typical sea waters (with salinity up-to 30 in the surface layer). Strong interannual variability in this area is well illustrated in Fig. 12, where profiles of hydrological parameters at the closely positioned stations are presented. In September 2003 it was station 20 with coordinates 70.001° N, 161.201° E, in September 2004 – station 67 (70.165° N, 161.270° E) and in September 2008 it was station 33 (70.168° N, 161.217° E). CS characteristics of surface and bottom layers at these stations are presented in Table 3.

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The direct river discharge into the East Siberian Sea, mostly by the Kolyma River, was maximum in the summer of 2004, and minimum in the summer of 2003; the highest discharge of the Lena River was registered in the summer of 2008 and the minimum was in the summer of 2003 (Table 4). At the same time, the river plume in the ESS as traced by the distribution of hydrological parameters, normalized A_T and CDOM, had maximum easterly extension in 2004 and minimum in 2008 (Figs. 5, 7, 8, 10). The zone of change in CO_2 flux direction had an extreme western position in 2008, and an extreme eastern position in 2004 (Fig. 9). No strong correlation between the volume of the river discharge and interannual dynamics of the CO_2 evasion/invasion areas in the coastal waters of the ESS was observed.

Another factor that determines the interannual dynamics of the CS in the ESS were the dominant atmospheric processes that were substantially different in 2003, 2004 and 2008 (Fig. 3). Dominant along-shore winds toward the east over the Laptev Sea and the ESS in the summer of 2003 transport the Lena River plume into the ESS. In the summer 2004 the wind field caused intensive propagation of river waters to the north and east in the ESS and CO_2 evasion area was at its maximum. In the summer of 2008 along-shore winds toward the west dominated over the ESS under the anticyclonic regime and resulted in an influx of more saline waters from the Chukchi Sea into the ESS. The Kolyma and Indigirka river runoff plumes were forced to move offshore and westward to the New Siberian Islands and the Laptev Sea. Despite the largest Lena River discharge in September of 2008 the low saline waters were blocked to the west of the ESS and the CO_2 invasion area was at its maximum (Fig. 9).

In spite of considerable annual variability of river discharge, the atmospheric pressure pattern was the main factor that determined the dynamics of CS of the ESS waters. It did not only effect the distribution of different source waters, but also the magnitude of coastal erosion. Offshore winds in 2004 with maximum speeds during the study period, along with high river discharges, resulted in the highest transport of suspended terrigenous (riverine and erosive) organic matter into the ESS (Dudarev et al., 2008). Concentration of SPM was at its minimum in 2008, when westward water transport

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occurred and input of eroded material to the ESS was the lowest. SPM values were about two times lower in surface layer and 4.5 times lower in the bottom layer relative to 2004. Note, that organic carbon content in SPM on average is 6–16.3% (Dudarev et al., 2003, 2006).

The highest absolute CO_2 flux values, calculated using a cubic dependence of gas transport formulation for the daily average wind speed (Wanninkhof and McGillis, 1999) were obtained in September 2004 (Fig. 9, Table 2), the time of maximum wind-speed and the highest values of $\Delta p CO_2$. The lowest absolute CO_2 flux magnitudes were found in September 2003 under the cyclonic atmospheric regime.

The CO_2 evasion values calculated for the ESS shelf in the summer (Table 2) have exceeded the values obtained both for the continental shelf of high latitudes and, in the majority of cases, for the tropical/subtropical seas (Chen and Borges, 2009). This fact proves the significant role of allochtonous eroded carbon in the exchange processes on the Arctic shelves with a predominantly heterotrophic nature as especially the western East Siberian Sea ecosystem.

Previous estimates of the net CO_2 flux have relied on indirect mass balance considerations (Lyakhin and Rusanov, 1983; Anderson et al., 1998ab; Fransson et al., 2001). All these annual rates of net CO_2 flux have considerable uncertainty. The data reported here represent the first direct air-sea CO_2 flux multi-year considerations for the ESS shelf. However, it should be noted that these represent a snap shot computation.

Based on the mean values of sea- air CO_2 fluxes ($1.6\,\mathrm{mmol\,m^{-2}\,day^{-1}}$, $10.2\,\mathrm{mmol\,m^{-2}\,day^{-1}}$ and $3.9\,\mathrm{mmol\,m^{-2}\,day^{-1}}$ for September 2003, 2004 and 2008, respectively, Table 2), the area of open water (Fig. 4) and position of CO_2 flux zero-contour (Fig. 9) we assess the emission of CO_2 from the ESS during the ice-free period. Thus, during the warm periods of 2003, 2004 and 2008 the diffusive CO_2 fluxes from sea to the atmosphere were 0.6×10^{12} g C, 3.3×10^{12} g C and 1.2×10^{12} g C, respectively. Taking into account that eastern part of the sea is a sink for atmospheric CO_2 and the mean air- sea CO_2 flux were $-0.8\,\mathrm{mmol\,m^{-2}}$ day-^{1}, $-1.7\,\mathrm{mmol\,m^{-2}\,day^{-1}}$ and $-1.8\,\mathrm{mmol\,m^{-2}\,day^{-1}}$ for September 2003, 2004 and 2008, respectively, the net CO_2

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evasion equals 0.5–3.3×10^{12} g C. Since sea-ice provides an effective barrier to gas exchange during the rest of the year and only minor air-sea gas exchange is allowed through leads and fractures in the sea-ice (Semiletov et al., 2004), this rate is rough equivalent to an annual flux. In September 2008 when Pacific-originating water was substantial in the ESS the potential CO_2 out-gassing was reported to ∼5.5×10^{12} g C (Anderson et al., 2009). This value can significantly change year-to-year in relation to input of eroded carbon determined by river runoff and meteorological regime. Thus net CO_2 flux to the atmosphere could be strongly enhanced during fall convection. Additional source of CO_2 into the East Siberian Arctic shelf waters might be oxidation of methane which is released to the atmosphere to similar magnitudes or higher than the CO_2 sea – air efflux (Shakhova et al., 2010ab) and it is expected that methane emission will increase dramatically in response to the recent warming the most pronounced in the Arctic.

5 Summary and conclusions

The coastal waters of the ESS are among the most dynamic of the arctic seas, with substantial interaction and transformation of waters of different sources. Water dynamics is driven by winds (direction and intensity) which are largely dependent from location of the surface atmospheric pressure anomalies (atmospheric active centers). This impact on water mass mixing and current pattern also influences the dynamics of the air-sea CO_2 exchange. The year to year dynamics in surface water $p$$CO_2$ as well as air-sea flux was very variable. During the period of observation the highest out-gassing of CO_2 was observed in September 2004, when atmospheric pressure field supported winds dominantly from the south. Thus the river waters were distributed throughout the ESS that supported a lateral transfer of organic and inorganic carbon from erosion and river runoff. This caused a combination of high air-sea $p$$CO_2$ gradients and high wind speed, resulting in a large out-gassing of CO_2 to the atmosphere. The high flux was also supported by the fact that in 2004 the largest river discharge into the ESS occurred.

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The maximum CO_2 uptake by the coastal waters of the ESS was observed in September 2008 when the wind pattern supported a significant inflow of high transparent water of Pacific origin to the eastern ESS. The hydrographic conditions supported a marine dominated ecosystem in the eastern EES with significant primary production resulting in consumption of CO_2 leading to low pCO_2. However, in 2008 the wind conditions were relatively calm resulting in a modest CO_2 uptake from the atmosphere. The average CO_2 air-sea flux values (both positive and negative) were the lowest in 2003 when the low atmospheric pressure field dominants over the adjacent Arctic Ocean.

This study of the CS, including the air-sea CO_2 fluxes, in the ESS supports the existence of two biogeochemical domains. Furthermore it shows the dominating heterotrophic character of the coastal zone, except for the time when the wind pattern cause substantial inflow of waters of Pacific origin.

The ESS shallow shelf as a whole is a net source of CO_2 into the atmosphere ranging from ~0.5 to 3.3×10^{12} g C. It may be strongly modulated by recent warming in the Arctic given the large stores of carbon in northern high latitude permafrost and positive feedbacks between temperature rise and terrestrial bio-available organic matter release onto the Arctic shelf.

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Table 1. Dates of cruises in the ESS.

Cruise	Date
Ivan Kireev 2003	12 September to 20 September
Ivan Kireev 2004	1 September to 14 September
Yakob Smirnitskiy 2008	29 August to 5 September
	9 September to 16 September

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Table 2. Averaged values of the difference in partial pressures of CO_2 between the surface water and atmosphere (ΔpCO_2) for the regions of under- (invasion) and over- (evasion) saturation relative to the atmosphere, the CO_2 flux for these two regions (F_{CO_2}), and the daily average wind speed (U), for all oceanographic stations visited in the ESS in 2003, 2004 and 2008.

Year	$\Delta pCO_{2\ inv}$ µatm	$\Delta pCO_{2\ ev}$, µatm	$FCO_{2\ inv}$, mmol m^{-2} day^{-1}	$FCO_{2\ ev}$, mmol m^{-2} day^{-1}	U m s^{-1}
2003	-44 ± 42, $n=9$	69 ± 47, $n=32$	-0.8 ± 0.8, $n=9$	1.6 ± 1.5, $n=32$	4.0 ± 0.8, $n=41$
2004	-35 ± 44, $n=4$	196 ± 103, $n=62$	-1.7 ± 2.1, $n=4$	10.2 ± 8.1, $n=62$	5.7 ± 1.7, $n=66$
2008	-90 ± 69, $n=24$	121 ± 154, $n=21$	-1.8 ± 1.4, $n=24$	3.9 ± 5.5, $n=21$	4.4 ± 1.3, $n=45$

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Table 3. Carbonate system characteristics of surface/bottom layers at stations 20, 67 and 33.

Station No	A_T, mmol kg^{-1}	pH$_{in\ situ}$, pH units	pCO$_2$, µatm
20	1.280/1.833	7.766/7.675	521/803
67	0.975/0.988	7.592/7.593	643/642
33	2.061/2.064	7.669/7.661	901/919

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Table 4. Average river discharge, $m^3 s^{-1}$, during the summer season (June–September).

Year	Lena River*	Kolyma River**
2003	38 990	6920
2004	48 564	9535
2008	49 829	7508

* data of http://rims.unh.edu
** data of Regional Tiksi Hydrometeorological Service

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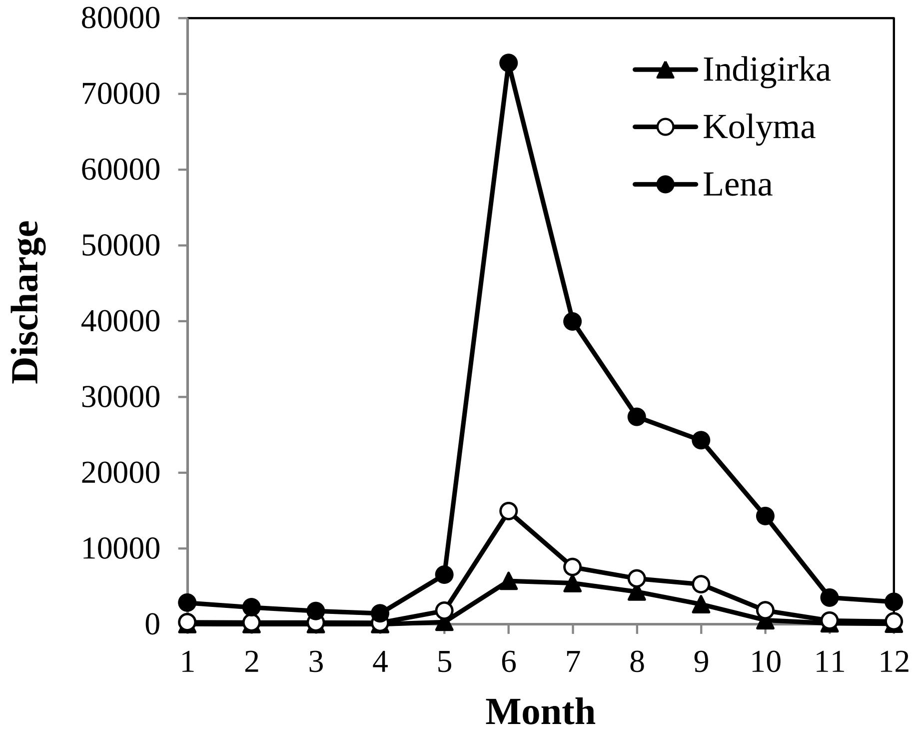

Fig. 1. Monthly average river discharge ($m^3 s^{-1}$).

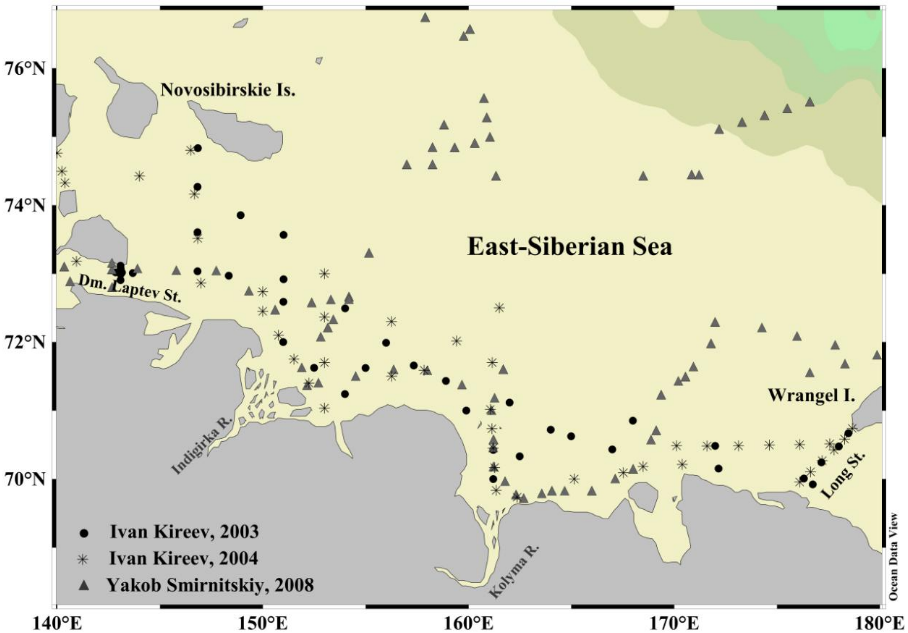

Fig. 2. Map of the stations in the East Siberian Sea during 2003, 2004 and 2008 surveys.

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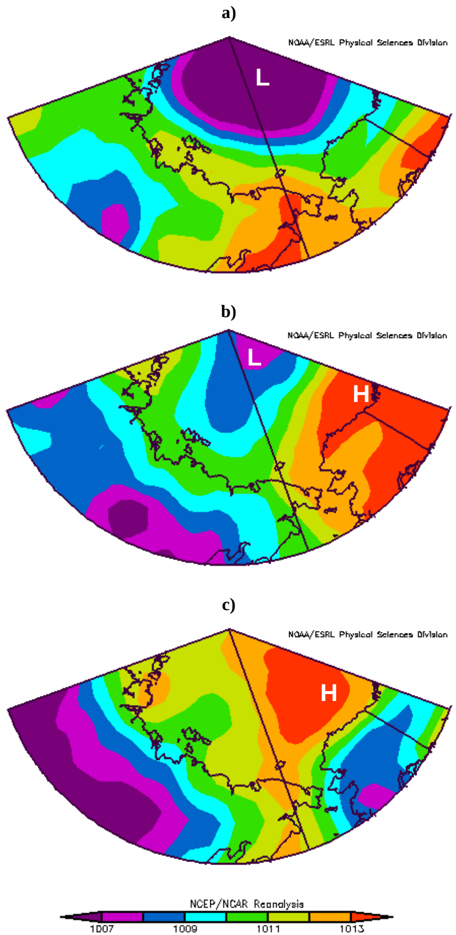

Fig. 3. Sea level pressure fields (mbar), averaged over summer season (July–September) of 2003 **(a)**, 2004 **(b)**, and 2008 **(c)**, from NCEP data.

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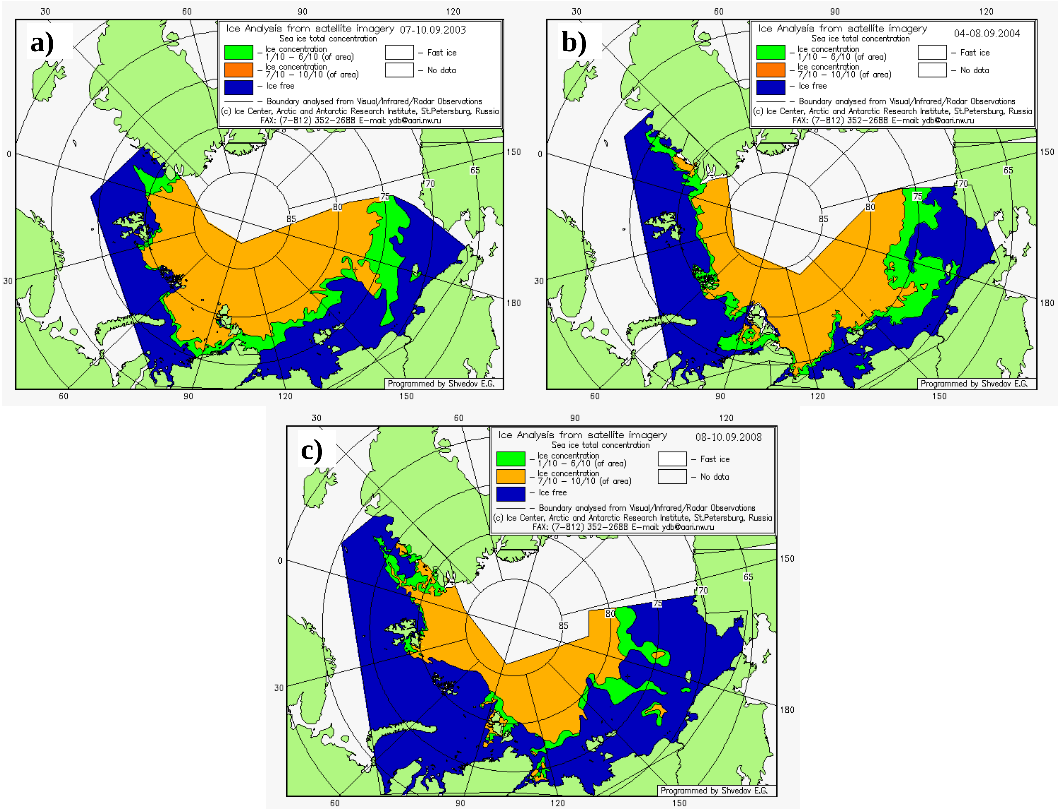

Fig. 4. Sea ice extent in the Eurasian Arctic Seas during expeditions dates: September 2003 **(a)**, 2004 **(b)** and 2008 **(c)**, from AARI data. Blue is open water, green is 1/10 to 6/10 ice coverage and orange is 7/10 to 10/10 ice coverage.

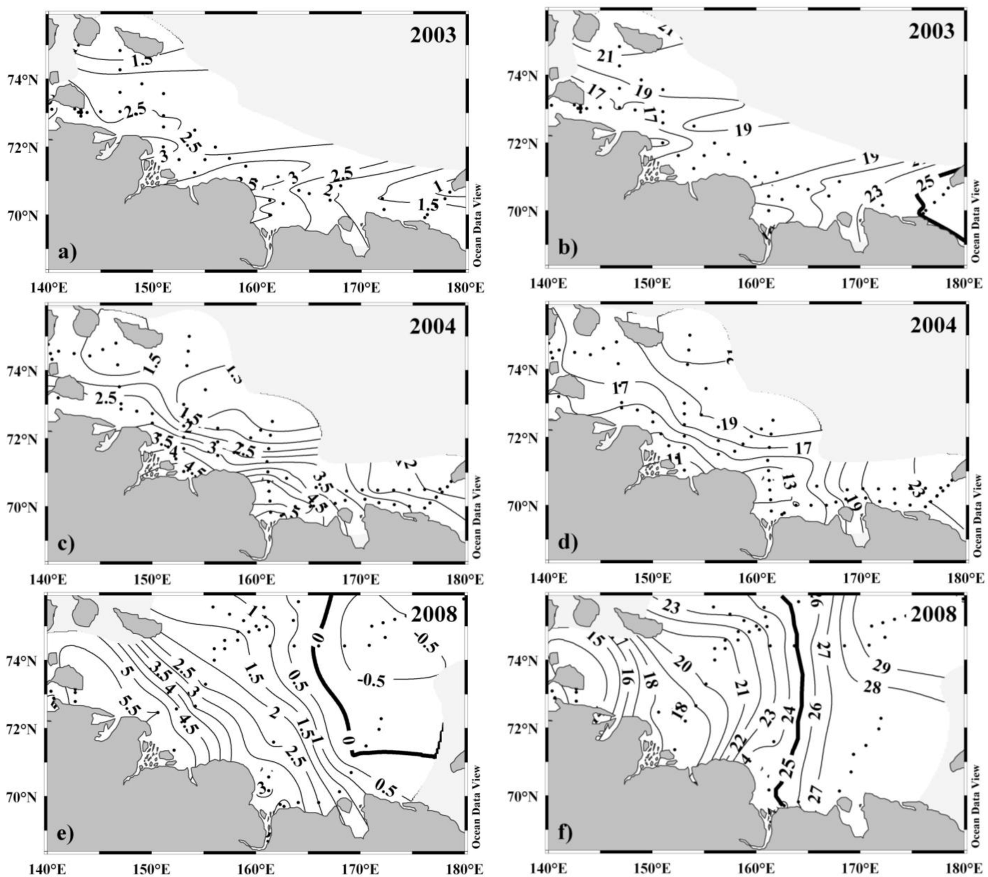

Fig. 5. Spatial distributions of sea surface temperature, T (°C) **(a, c, e)** and salinity, S **(b, d, f)** in the ESS during 2003, 2004 and 2008 surveys.

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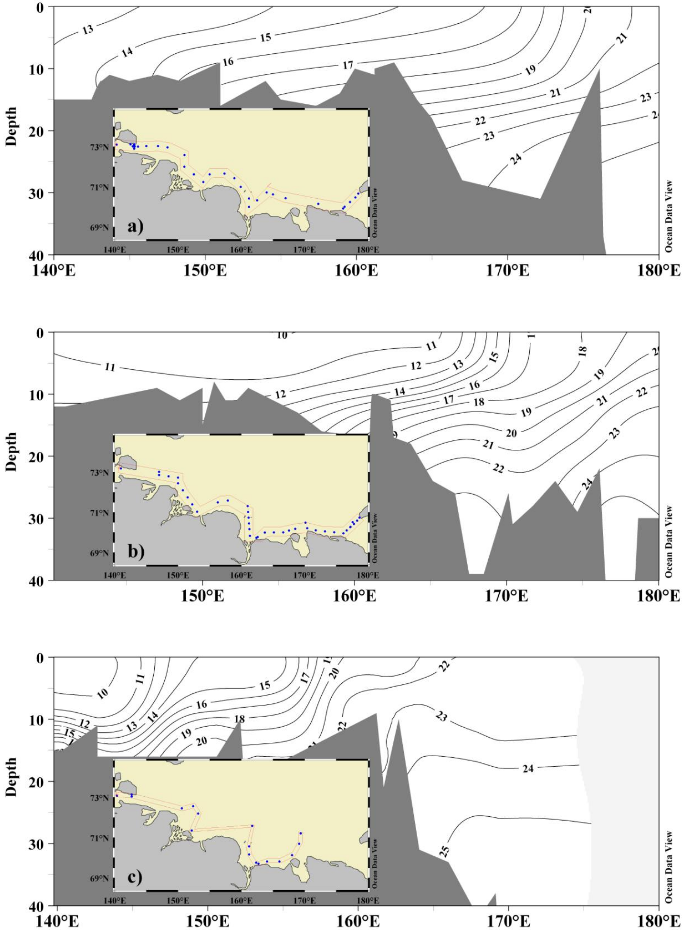

Fig. 6. Profiles of density (kg m^{-3}) on the alongshore transects in September 2003 **(a)**, 2004 **(b)** and 2008 **(c)**.

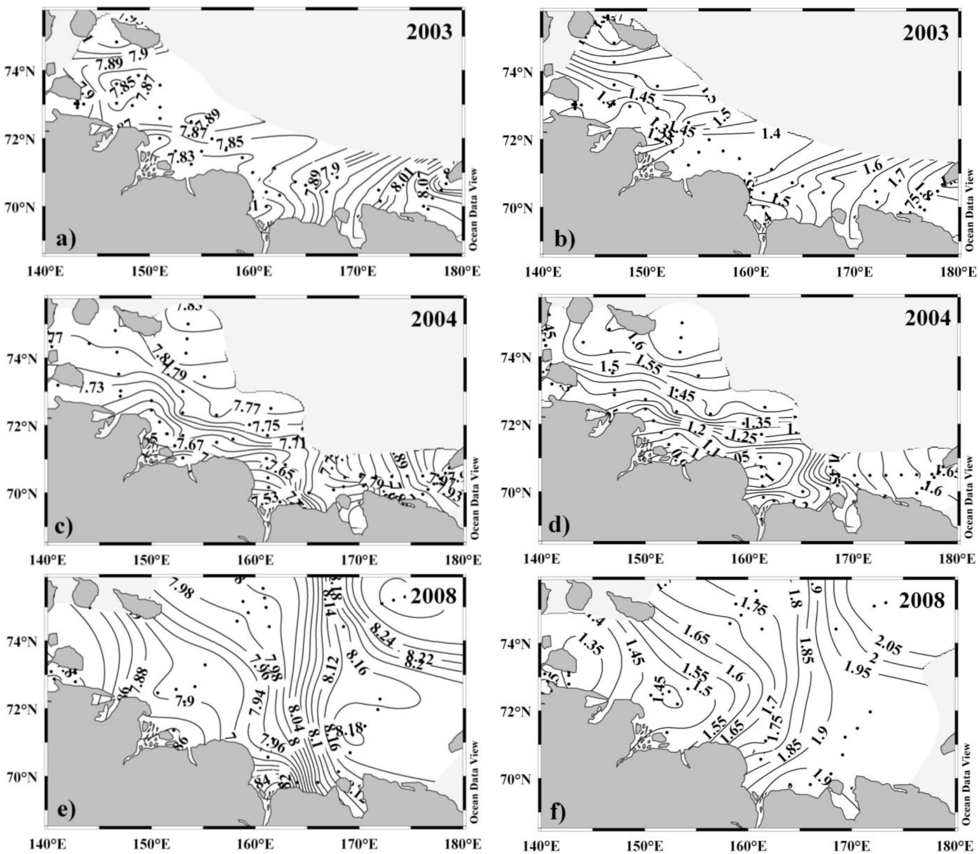

Fig. 7. Spatial distributions of surface $pH_{in\ situ}$ **(a, c, e)**, and total alkalinity, A_T ($mmol\,kg^{-1}$) **(b, d, f)**, in the ESS during 2003, 2004 and 2008 surveys.

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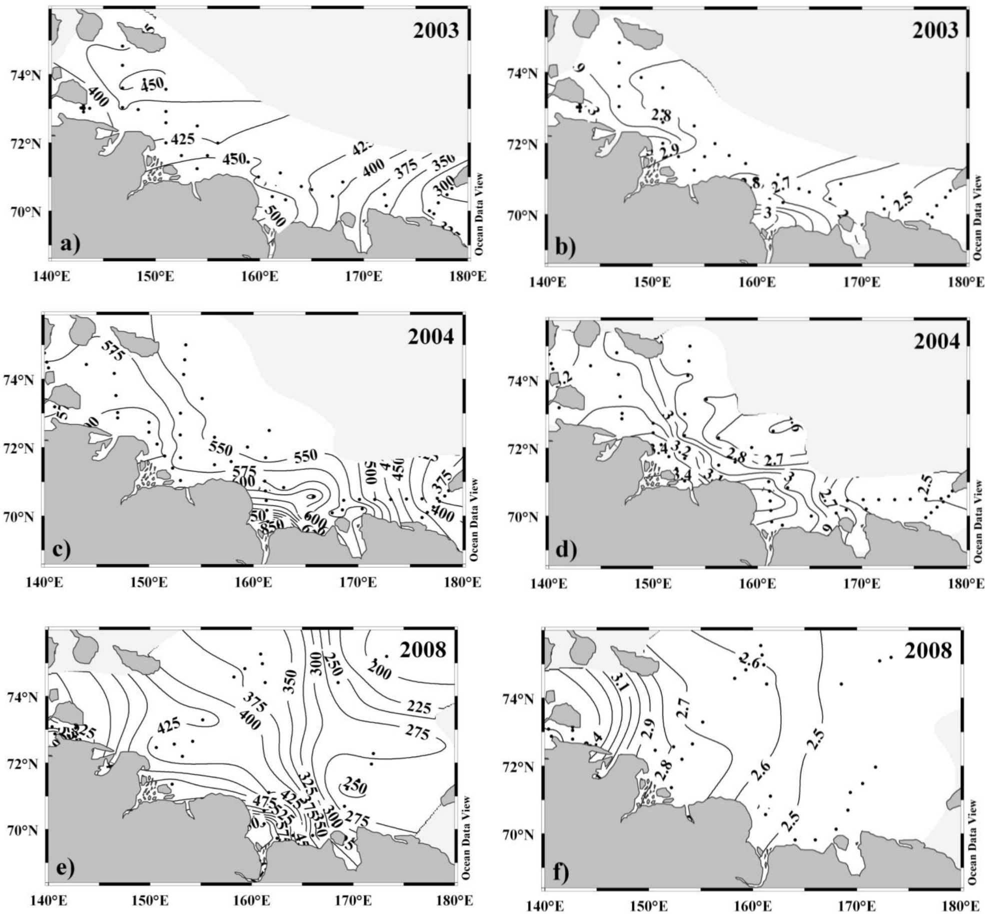

Fig. 8. Spatial distributions of surface pCO_2 (µatm) **(a, c, e)** and normalized total alkalinity, nA_T (mmol kg^{-1}) **(b, d, f)**, in the ESS during 2003, 2004 and 2008 surveys.

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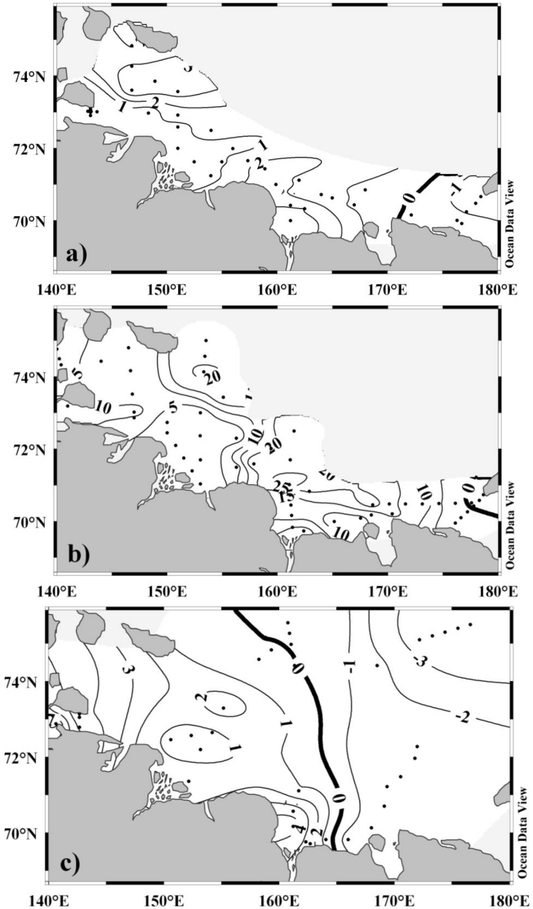

Fig. 9. Spatial distributions of CO_2 fluxes (mmol m^{-2} day^{-1}) over the ESS shelf during 2003 **(a)**, 2004 **(b)** and 2008 **(c)** surveys.

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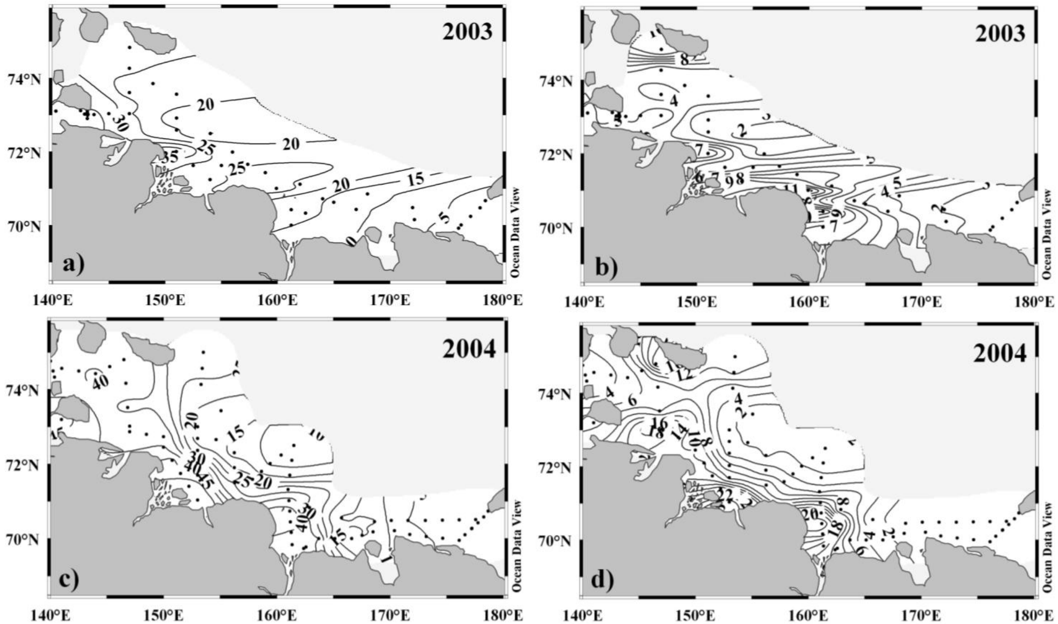

Fig. 10. Surface spatial distributions of CDOM ($\mu g\, l^{-1}$) **(a, c)** and SPM ($mg\, l^{-1}$) **(b, d)** over the ESS shelf during 2003, 2004 surveys.

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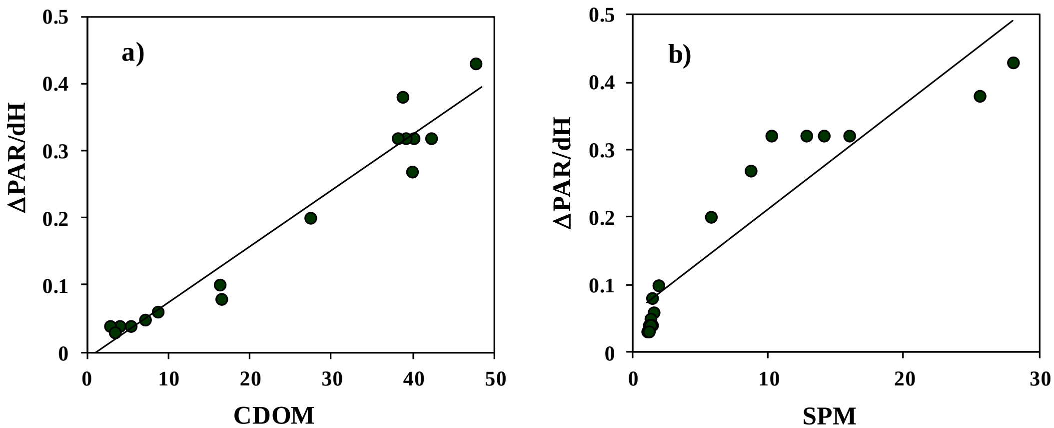

Fig. 11. Correlation of the PAR extinction in layer H_5 versus CDOM ($\mu g\,l^{-1}$) **(a)** and SPM **(b)** ($mg\,l^{-1}$).

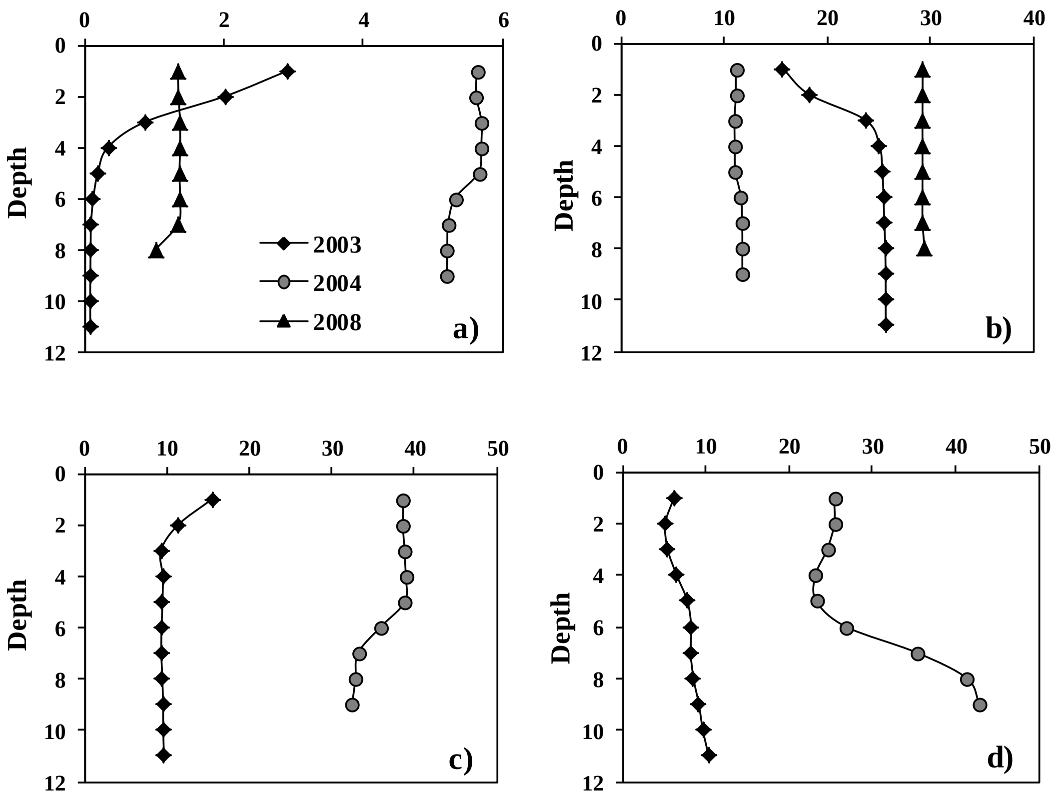

Fig. 12. Profiles of temperature, T (°C) **(a)**, salinity, S **(b)**, CDOM ($\mu g\, l^{-1}$) **(c)** and turbidity (NTU) **(d)** at the nearest stations in September 2003, 2004 and 2008.

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