The Kara Sea Expedition of RV "Akademik Boris Petrov" 1997: First Results of a Joint Russian-German Pilot Study

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TABLE OF CONTENT

PREFACE

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The Arctic Ocean can be considered a giant estuary fed by rivers draining a significant part of the Eurasian continent and of North America. A major amount of this fresh water stems from the Russian rivers Pechora, Ob, Yenisei and the Lena. Freshwater input from these rivers together with meltwater from Arctic glaciers and ice sheets is of critical importance in influencing the global climate system since formation of deep water masses in the North Atlantic as a major climatic driving force is heavily dependent on salinity variations derived from the Arctic Ocean.

The Siberian rivers together with their adjacent shelf seas represent also an important part of a bio-geochemical system within which extensive interaction between continent and ocean is a significant component.

The sediments accumulating in the Arctic Ocean basins and shelf seas are rich in organic matter. Virtually nothing is known about the sources of this organic matter - terrestrial or marine - and on the processes that have led to its accumulation. A better understanding of these factors is necessary to assess the role of the Arctic Ocean as a potential sink for carbon dioxide. The sediments of the Arctic shelf seas are well known to represent significant sources of climatically relevant gases such as methane which is released at the sea floor.

At present, the Arctic region faces two most serious ecological problems. The first one is related to the discovery of huge gas and oil resources. The hydrocarbon reserves on the shelves are estimated at tens of trillions of cubic meters of gas and tens of billions of metric tons of oil what equals to about a quarter of the world´s hydrocarbon reserves. The prospect of an intense economic development in the Arctic region requires the knowledge of the bio-geochemical background as the principal basis for handling and managing principal environmental issues.

Another serious problem is a potential radioactive pollution of the Arctic Ocean and particularly the Kara Sea due to fallout from nuclear testing activities and radioactive wastes from various sources. The distribution and behavior of radionuclides in the ocean is determined by their sources and a number of geochemical factors such as composition of particulate matter, conditions of reworking of the organic substance, the resulting redox conditions in the sediments and the hydrophysical parameters of the sea water.

To get a better idea of the relevant modern processes being active in this continent-ocean system along a strong salinity gradient from the Ob and Yenisei estuaries, over the shallow shelf of the eastern and northern Kara Sea and continental slope into the open Arctic Ocean and to answer the various questions mentioned above, a bilateral Russian-German multi-disciplinary programme has been defined. As a first step and pilot study a scientifically very successfull joint Russian-German research expedition into the estuaries of rivers Ob and Yenisei and to the adjacent Kara Sea shelf was carried out during summer 1997 using RV "Akademik Boris Petrov" of the Vernadsky Institute of Geochemistry and Analytical Chemistry. It is expected that the promising results of this first joint expedition into the Kara Sea will foster Russian-German scientific collaboration in this area and will help to successfully implement a scientifically sound research project on the continent-ocean system.

ПредИисповие

Северньгй Педовитъый океан может рассматриватъся как гигантская эстуария питаемая реками, дренируюшими обширную территорию Евразии и Северной Америки. Ъолъшая часть пресной воды доставляется российскими реками Печорой, Обью, Енисеем и Пеной. Масса пресной воды, поступающая с зтими реками, а также образующаяся в результате таяния арктических глетчеров и покровного льда, оказывает опредляющее влияние на глобальную систему климата поскольку формирование глубинных вопных масс в Северной Атпантике - главная лвигающая сила климата - зависит от вариаций солености, задаваемых Арктическим бассейном.

Сибирские реки вместе с соответствуюшими шельфовыми морями представляют также важнуо часть биогеохимической системы, в пределах которой осуществляется широкое взаимодействие между океаном и континентом.

Осадки, аккумулирующиеся в Северном Ледовитом океане и шельфовых морях богаты органическим веществом. Фактически ничего неизвестного об источниках зтого органического вещества - континентального ипи морского - и процессах, которые привели к его аккумуляции. Знание зтого необходимо дпя оцекни роли Северного Ледовитого океана в качестве потенциального стока атмосферной лвуокиси углерода. Хорошо известно, что осадни Арктических шельфовых морей представляют важный источник газов, влияющих на климат, таких как метан, выделяюшийся со дна океана.

В настояшее время Арктический регион сталкивается с двумя наиболее серьезными зкологическими проблемами. Первая связана с открытием огромных ресурсов нефти и газа. Запасы утлеводородов на шепьфе оцениваются в десятки триллионов кубических метров газа и десятки миллиардов тон нефти, что составляет почти четверть мировых запасов утлеводородного сырья. Перспективы интенсивного зкономического развитии Арктического региона требуют изучения современного биогеохимического фода как принципиальной осноы дпя организации контроля и управления в вопросах охраны окружающей среды.

Другая серьезная проблема - опасность радиоактивного загрязнения Актического бассейна, в особенноoти Карского моря, продуктами ядерных испытаний и радиоактивными отходами из разных источников.

Распределение и поведение радионуклидов в океане определяется их источниками и рядом геохимических факторов, таких как состав взвешенного материала, условиями переработки органического вешества, окислительно-восстановительным режимом в осадках и гидрофизическими параметрами водной толщи.

Для того, чтобы лучше понять соответствуюшие современные процессы, идушие в зтой системе континент-океан, и ответить на вопросы, упомянутые вьппе, определена двусторонняя Российско-Германская программа исследований в Арктическом бассейне вдоль градиента солености от зстуарий Оби и Енисея через мелководный шельф, север Карского моря и континентальный склон к открытому океану. В качестве первого предварительного шага летом 1997 года была предпринята оказавшаяся весьма успешной в научном отношении совместная Российско-Германская зкспедция вдоль зстуарий рек Обь и Енисей и прилегающей части шельфа Карского моря на НИС "Академик Борис Петров", принадлежащим Институту геохимии и аналитической химии им. В.И.Вернадского Российской Академии наук. Спедует ожидать, что многообещаюшне результаты зтой первой совместной зкспедиции в Карское море укрепят Российско-Германское сотрудничество в зтой областн и помогуг успешному осуществлению значимого в научном отношении проекта изучения системы океан-континент.

THE EXPEDITION TO THE KARA SEA IN SUMMER 1997: SUMMARY OF THE SHIPBOARD SCIENTIFIC RESULTS

Matthiessen, J., Stepanets, O.V. and the shipboard scientific party*

Introduction

The expedition with RV "Akademik Boris Petrov" to the Kara Sea was conducted from August 21 to October 8, 1997 in the framework of a joint project of the Vernadsky Institute of Geochemistry and Analytical Chemistry in Moscow and the Alfred Wegener Institute for Polar and Marine Research in Bremerhaven (Fütterer and Galimov, this volume; Matthiessen and Stepanets, 1998). The project "The Nature of Continental Run-off from the Rivers Ob and Yenisei and its Behaviour in the adjacent Kara Sea" aims at investigating geological, biological and biogeochemical processes in the estuaries of the Siberian rivers Ob and Yenisei and the adjacent Kara Sea (Fig. 1). Several major research topics were identified which should be studied:

- Nature of river supply into Kara Sea
- Modification of fluvial output in the estuaries of rivers Ob and Yenisei
- Dispersal and deposition pattern of river supply and its distribution in the Kara Sea
- Variations of coastal marine processes in relation to river supply
- Responses of the benthic system to changes at the sea surface
- Dispersal and distribution pattern of contaminants
- Gas release and its distribution pattern on the Kara Sea shelf
- Reconstruction of the Holocene and Late Glacial paleoenvironments in the Kara Sea

This volume of Reports on Polar Research comprises the initial results which were obtained on water column, surface and near-surface sediment samples collected during the cruise and on selected material of other cruises which are of relevance for obtaining the scientific goals of the project. In this paper we shortly describe the environmental setting of the investigation area and summarize the scientific results of the cruise. Details of the sampling and scientific programs are described in the cruise report (Matthiessen and Stepanets, 1998).

Influence of the rivers Ob and Yenisei on the environment

The investigation area is located in the eastern Kara Sea from the bays of the rivers Ob and Yenisei to latitude 74°N (Fig. 1), where strong seasonal freshwater influx influences the marine environment. The Kara Sea has a size of about 883,000 km^2 and receives about one-third of the total freshwater entering the Arctic Ocean and about 55% (1290km^3/year) of the total continental run-off to the entire Siberian Arctic (e.g. Pavlov and Pfirman, 1995). The rivers Ob and Yenisei contribute about 80% of the run-off to the Kara Sea. The Ob has the largest catchment area and length and the Yenisei has the greatest discharge volume of Siberian rivers (Telang et al., 1991). The characteristic

*see Appendix 1

geographical and hydrochemical features of both rivers are summarized and compared with those of the Lena River in Table 1.

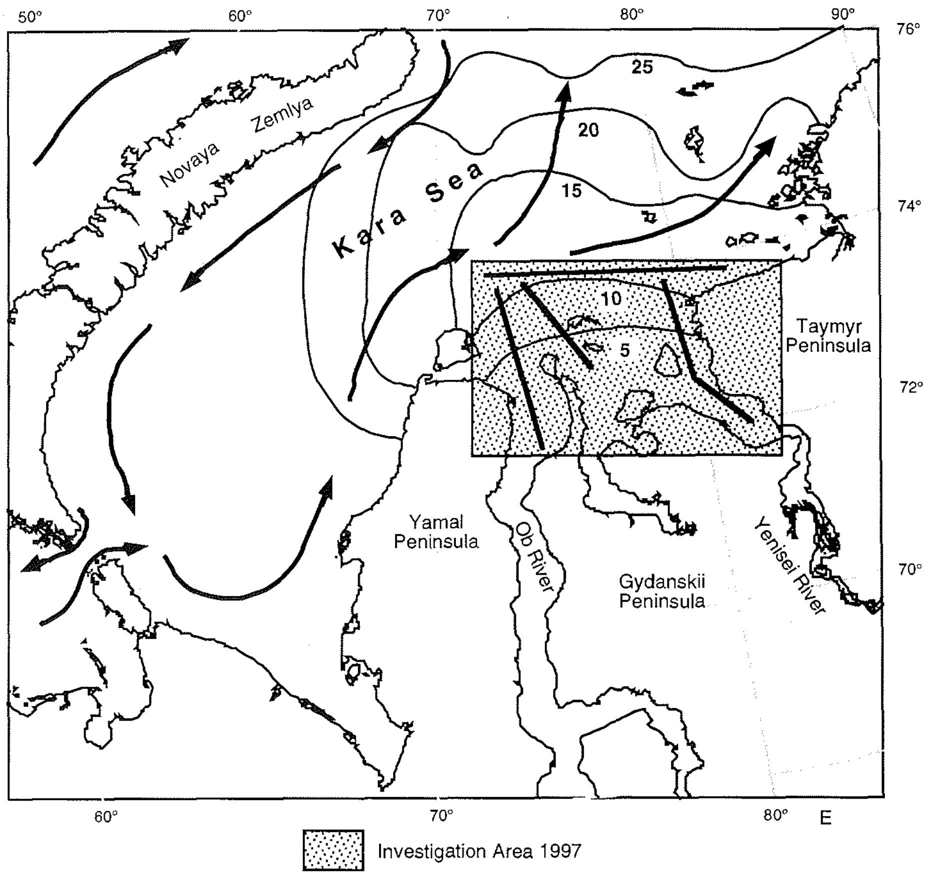

Fig. 1. Location of the investigation area in the southeastern Kara Sea with schematic surface circulation (Pavlov and Pfirman, 1995). The mean distribution of sea-surface salinities is based on measurements in August and September (Burenkov and Vasilkov, 1995). Lines indicate the transects.

The catchment areas of Ob and Yenisei differ distinctly. The Ob is a typical river of the plains, and flows through taiga forest, the forest tundra zone and tundra. The Yenisei drains in the upper and middle reaches mountain areas with rocky banks, covered with taiga and small strips of forest steppe. In the lower reaches it is a plain river flowing through taiga and forest tundra (Telang et al., 1991).

The river run-off shows a strong seasonal and interannual variability. The Ob and Yenisei discharge continuously into the Kara Sea throughout the year, but the maximum discharge is observed in June when the coastal zone is still ice-covered (Fig. 2). In the flood period from May to July 45 to 65% of the annual river run-off (Gordeev et al., 1996) and about 80% of the annual dissolved and

Table 1. Major characteristics of the Siberian rivers Ob, Yenisei and Lena.

	catchment Area (1) 10^6 km^2	length (1) km	annual discharge (2) km^3	suspended matter 10^6 t a^{-1}	dissolved matter (1) 10^6 t a^{-1}	TOC fluxes (2) 10^6 t a^{-1}
Ob	2,99 x 10^6	3650	429	16.5 (2) 13.4 (1)	34.0	3.05
Yenisei	2,58 x 10^6	3844	620	5.9 (2) 14.5 (1)	43.2	4.59
Lena	2.47 x 10^6	4337	525	17.6 (2) 11.7 (1)	41.3	5.3

(1) Telang et al. (1991); Ob: from source of Irtish 5410 km, and with Ob inlet 6370 km
(2) Gordeev et al. (1996)

suspended matter supply is discharged (Lisitzin, 1995). Despite the large freshwater supply, mean sediment concentrations in e.g. the Ob is much lower than in the Mackenzie River, probably because of the large flood plains which are large sinks of sediments (Smith and Alsdorf, 1998). However, the total organic carbon contents of these Siberian rivers are as high as that of the Mackenzie River (Telang et al., 1991), showing that they are important sources for organic carbon in the shelf seas and Arctic Ocean. The investigation area is located in the "marginal filter" where next to the flood plains and deltas of Ob and Yenisei most suspended and dissolved load of the rivers is deposited (Lisitzin, 1995). The expedition to the Kara Sea was carried out in September/ October 1997 distinctly later than the peak discharge of freshwater into the Kara Sea (Fig. 2).

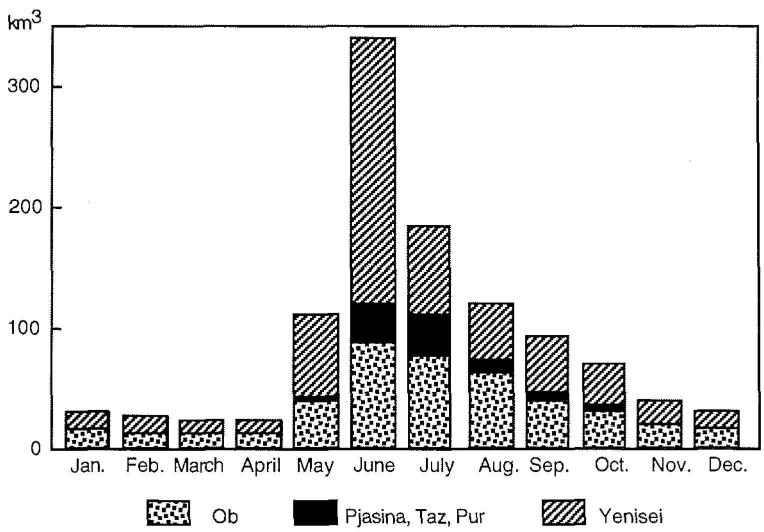

Fig. 2. Mean river discharge to the Kara Sea (from Pavlov and Pfirman, 1995).

The investigation area is influenced by river water during the summer months (Burenkov and Vasilkov, 1995). This is reflected in the low mean sea-surface salinities (<15psu) in summer, while sea-surface temperature can range from 4 to 9°C. The freshwater spreads on the surface layer into the Kara Sea and is distributed by the Yamal Current mainly to the north and northeast to the Arctic Ocean and through the Vilkitsky Strait to the Laptev Sea (Pavlov and Pfirman, 1995). The cyclonic circulation pattern in the Kara Sea is driven by the prevailing winds.

The investigation area was free of sea ice during the second half of September when the station work was conducted in the Ob and Yenisei bays. The Kara Sea is usually ice covered from October to May (Pavlov and Pfirman, 1995). Fast sea ice covers the coastal zone and the estuaries and bays of Ob and Yenisei during the winter months until July. The rivers usually break up in the upper course in April and in the lower reaches in June. The north-central and eastern Kara Sea is next to the Laptev Sea an important source area for sediment laden sea ice which is transported in the Siberian branch of the Transpolar Drift to Fram Strait (Pfirman et al., 1997).

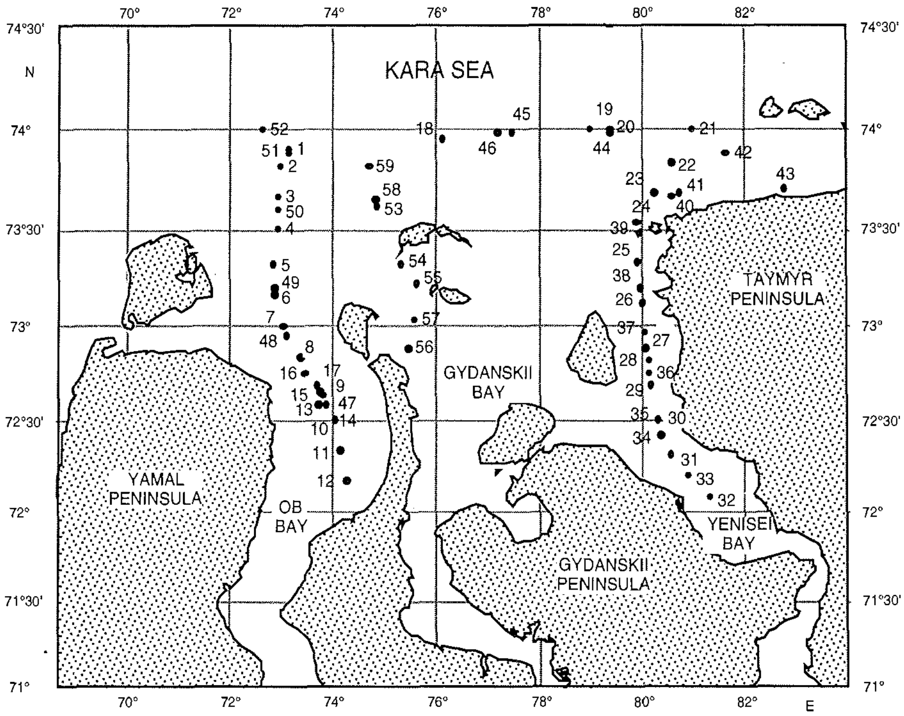

Fig. 3. Sampling stations of the 28th cruise of RV *Akademik Boris Petrov* (52 = BP97-52).

Concept of investigations

Several major expedition were already conducted in the Kara Sea (e.g. "Professor Shtockman" in 1984, see Levitan et al., 1996; RV "Dmitry Mendeleev" in 1993, Lisitsyn and Vinogradov, 1995; RV "Akademik Boris Petrov" in 1995, Galimov et al., 1996) leading to a better understanding of the biological, geochemical and geological processes in the whole Kara Sea. The expedition in 1997 concentrated on the outer Ob and Yenisei estuaries where the mass of the dissolved and suspension load is deposited in the "mixing zone" (Lisitsyn, 1995). The water column and sediments were sampled on 59 stations along transects in the Ob, Yenisei and Gydanskii bays as well as along latitude 74°N (Figs. 1, 3; Appendix 2). In particular on the transects in Ob and Yenisei, biological, biogeochemical and geological processes were studied along the salinity gradient. Some scientific programs were already initiated during the 22th cruise of RV "Akademik Boris Petrov" in 1995 (Galimov et al., 1996). A large data set about physical and chemical characteristics of the water column was already obtained during the cruise while only few analyses could be conducted on the sediments. The long sediment cores are stored in the core repository of AWI. They will be opened, described and sampled in a later phase of the project.

Because special emphasis was placed on studying modern processes in the estuaries, CTD measurements were performed first on all stations to get an overview of the water column structure. Sampling depths were chosen according to salinity and temperature profiles. On water column stations water samples were taken from the following depths: surface layer, deep surface (depending on the thickness of the mixed layer), above the pycnocline, below the pycnocline and deep water (close to bottom).

Depending on the CTD results, various sampling programs were conducted. Both the water column and sediments were extensively sampled on 21 main stations along the four transects for all scientific programs (Fig. 4). Additionally, sediment traps were deployed at four stations. For biological and geochemical programs bottom sediments were sampled at additional stations. Finally, at selected stations, sediment cores up to a length of ca. 5 m were recovered (Fig. 5).

Table 2. Definition of water masses (from Churun and Ivanov, 1998a).

Water type	Ob estuary		Yenisei estuary	
	T [°C]	S [psu]	T [°C]	S [psu]
MW	up to 6.3	<3.1	up to 8.0	< 1.9
TMW	4.4 - 5.4	7.6 - 13.1	6.1 - 6.8	5.7 - 11.8
PWKS	-0.1 - -1.5	30.7 - 32.3	-0.7 - -1.2	30.9 - 31.9
TPWKS	0.8 - 2.2	20.2 - 25.0	4.2 - 5.6	9.9. - 17.9

MW - meteoric water (Ob River or Yenisei River plus precipitation);
TMW - transformed meteoric water;
PWKS - polar water of the Kara Sea;
TPWKS - transformed polar water of the Kara Sea.

Shipboard scientific results

Water column investigations

Temperature, salinity and oxygen content of the water column were measured on all stations in particular in the bays of Ob and Yenisei (Churun and Ivanov, 1998a), where hydrographic transects were run twice. All stations were located in the freshwater plume of Ob and Yenisei. Therefore, the water column was characterized by a strong stratification during the cruise. The mixed layer (thickness of ca. 5 to 8 m) consisted of either meteoric water (MW: river water plus precipitation) or transformed meteoric water (TMW) which is a mixture of meteoric water and saline surface water of the Kara Sea (Table 2). MW was restricted to the inner bays of Ob and Yenisei, whereas TMW covered the surface waters of the outer bays and the inner Kara Sea. The transition from MW to TMW occurred more or less continuously but steep gradients existed in the Ob Bay between September 13-15, when a local frontal zone developed with strong gradients in temperature (0.07°C/km) and salinity (0.3psu/km). These changes in surface water conditions were principally related to a decrease in water depth. The transparency of the upper water column was slightly higher along the 74°N transect than in the Ob and Yenisei bays (Churun and Ivanov, 1998b).

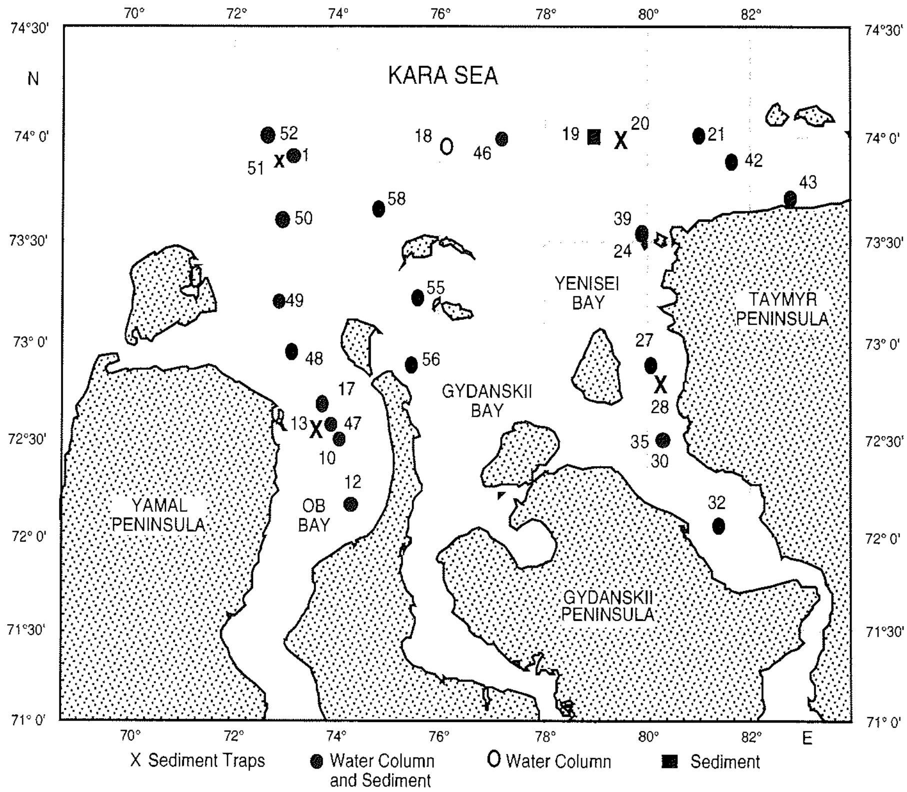

Fig. 4. Major water column and sediment sampling stations (52 = BP97-52).

Below the pycnocline with a thickness of 4-8m the physical properties of the water column were relatively uniform (Churun and Ivanov, 1998a). The deep water is composed of polar winter water of the Kara Sea (PWKS) which had a salinity >30psu and temperatures below 0°C. It was modified in the southern shallower parts of the bays where it mixed with MW forming a thin layer of transformed polar winter water of the Kara Sea (TPWKS) at the sea bottom.

Hydrochemical and radio-geochemical parameters measured on board showed a strong relationship to the salinity gradient in surface waters. Total alkalinity, total dissolved inorganic carbonate and ph values increased with increasing surface water salinity (Shpigun, 1998). The same holds true for the distribution of the radionuclide ^{137}Cs. Concentrations increased with increasing salinity (Stepanets et al., 1998). In contrast the methane concentrations were inversely related to the salinity gradient along the Ob transect (Samarkin, 1998).

The preliminary results of zooplankton investigations suggest that the hydrophysical structure of the water column is reflected in the distribution of copepods. The low salinity surface waters contained a fauna of brackish to freshwater species, whereas in the deep waters marine species prevailed (Halsband, 1998).

Surface and near-surface sediment investigations

Surface sediments and sediment cores were especially collected on the main stations along the transects where the water column was extensively sampled for biological and biogeochemical analyses (Fig. 4). Apart from visual description, smear slide analyses gave first information about the mineralogial composition. The surface sediments are usually fine-grained, ranging in grain size from silty clays to clayey silts. There is a trend to coarser sediments along the transects from the Ob and Yenisei bays to 74°N which may be attributed to the deposition of fines in the bays and an influx of sand from the coastal zone of the Kara Sea. Brownish sediment colours are usually restricted to the upper 1 to 3 cm. Diatoms are the dominant biogenic component in surface sediments, increasing in abundance with decreasing surface water salinity (Matthiessen et al., 1998).

Surface sediments contained a fauna composed of polychaetes and rare occurrences of isopods and brittle stars. Initial results on benthic foraminifera analyses suggested that assemblages from the bays might differ considerably from the inner Kara Sea despite comparable bottom water salinities (Korsun, 1998). This is probably related to the disturbed habitats because of e.g. strong freshwater and sediment influx.

Near-surface sediments were recovered by box and multi corer (recovery 20 to 50cm). Sediments are relatively monotonous consisting of clays to silty clays with few sandy layer. Grain-size is slightly increasing northward along the transects. Occassionally, plant debris and wood fragments have been found. Macrofossils occur scattered in the sediment columns.

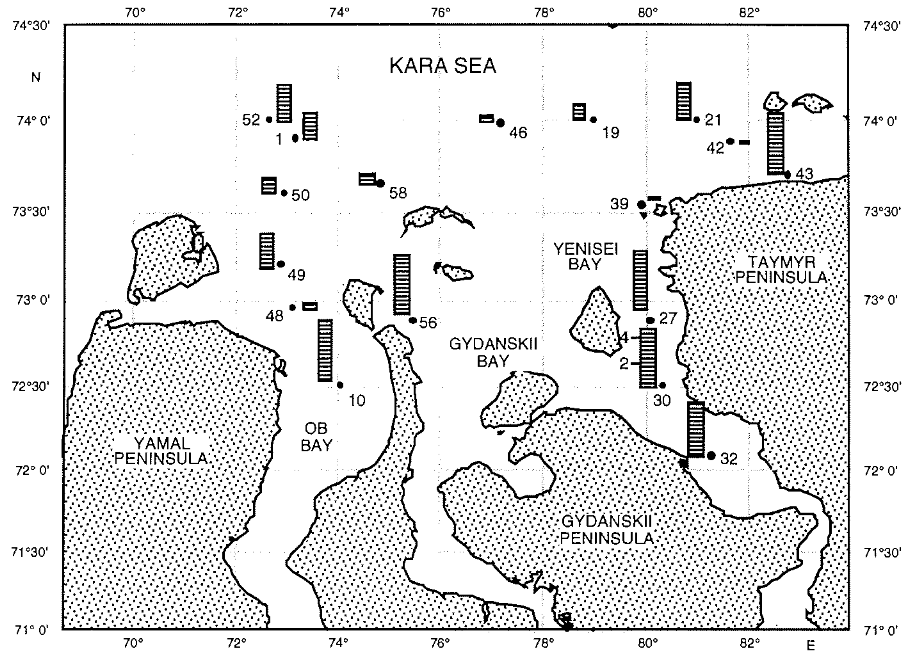

Fig. 5. Length of sediment cores obtained during the cruise. Scale (m) see sediment core at station 30 (= BP97-30).

Few geochemical data were obtained during the cruise. There is some evidence for organic matter degradation derived from shipboard measurements of redox potential, sediment colour, density and TCO_2 concentrations in pore water indicating that reductive processes start from ca. 4 to 7 cm sediment depth (Kodina et al., 1998). Brownish yellow crystals composed of $CaCO_3$ $*6H_2O$ probably being ikaite have been found in the Yenisei Bay (St. 24). Methane analysis in near-surface sediments from the Ob transect revealed that concentrations increased from the inner Kara Sea to the estuary (Samarkin, 1998). The radionuclide ^{137}Cs displays an irregular distribution in surface sediments with principally higher concentrations in the Yenisei Bay (Stepanets et al., 1998). Heavy metal contents and concentrations strongly changed in the uppermost cm, e.g. in Mn and Br contents, which are related to the oxidation in near-surface sediments (Krasnyuk, 1998).

Sediment cores (gravity cores) have been successfully recovered from 15 stations, ranging in length from a few cm to almost 500cm (Fig. 6). There is an obvious relationship between core length and sedimentary environment (Matthiessen et al., 1998). The longest cores were taken in the bays of Ob and Yenisei where sedimentation rates are probably much higher due to the preferential deposition of fluvial transported fine-grained sediments. These preliminary sedimentological investigations suggest that the investigation area which is located in fazies subzone IIB of Levitan et al. (1996) consists of two different sedimentary provinces.

Acknowlegements

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Appendix 1. Scientific participants of the 28th cuise of RV "Akademik Boris Petrov".

Stepanets	Oleg	Chief of Expedition	GEOKHI
Matthiessen	Jens	Co-chief Scientist, Geology	AWI
Borisov	Alexandr	Radio-Geochemistry	GEOKHI
Boucsein	Bettina	Geology	AWI
Braun	Barbara	Geology	AWI
Churun	Vladimir	Oceanography	AARI
Deubel	Hendrik	Biology	AWI
Dyadyk	Alexandr	Chemistry	GEOKHI
Finkenberger	Bettina	Geology	GEOMAR
Halsband	Claudia	Biology	AWI
Henne	Andreas	Marine Chemistry	IFBM
Ivanov	Boris	Oceanography	AARI
Khorshev	Victor	Engineer	GEOKHI
Kodina	Lyudmila	Organic Geochemistry	GEOKHI
Korsun	Sergey	Biology	MMBI
Krasnyuk	Alexander	Geochemistry	VNIIO
Lukashin	Vyacheslav	Geology	IORAS
Miroshnikov	Alexey	Geology	IGEM
Müller	Claudia	Geology	AWI
Neumann	Kirsten	Marine Chemistry	IFBM
Osadchiy	Nikoley	Engineer	GEOKHI
Petrunin	Leonid	Hydro-Geochemistry	VNIIO
Poltermann	Michael	Biology	AWI
Pribylova	Tatyana	Organic Geochemistry	GEOKHI
Prusakov	Boris	Computer Center Engineer	GEOKHI
Richter	Rainer	Marine Chemistry	AWI
Rusakov	Valeriy	Geology	IORAS
Samarkin	Vladimir	Geochemistry	ISSP
Schoster	Frank	Geochemistry	AWI
Shmelkov	Boris	Computer Center Engineer	GEOKHI
Shpigun	Liliya	Marine Chemistry	IGIC
Siebold	Martina	Organic Geochemistry	AWI
Solovyova	Galina	Radiochemistry	GEOKHI
Steffen	Sönke	Marine Chemistry	IFBM
Tokarev	Victor	Organic Geochemistry	GEOKHI
Vlasova	Lyudmila	Organic Geochemistry	GEOKHI

AARI	The State Research Center - Arctic and Antarctic Research Institute
AWI	Alfred Wegener Institute for Polar and Marine Research
GEOKHI	Vernadsky Institute of Geochemistry and Analytical Chemistry
GEOMAR	Research Center for Marine Geosciences
IFBM	Institute for Biogeochemistry and Marine Chemistry
IGEM	Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry
IGIC	Kuznakov Institute of General and Inorganic Chemistry
IORAS	Shirshov Institute of Oceanology
ISSP	Institute of Soil Science and Photosynthesis
MMBI	Murmansk Marine Biological Institute
VNIIO	VNIIOkeanologia, All-Russian Research Institute for Geology and Mineral Resources

Appendix 2. Station list with geographic coordinates.

Station	Latitude °N	Longitude °E	Depth (m)	Station	Latitude °N	Longitude °E	Depth (m)
BP97-01	73°54'38.0"	73°10'59.0"	31	BP97-31	72°19'48.6"	80°35'04.8"	13
BP97-02	73°49'56.0"	73°00'06.0"	30	BP97-32	72°05'35.4"	81°28'52.2"	10
BP97-03	73°40'04.0"	72°57'03.0"	28	BP97-33	72°12'43.2"	80°55'06.6"	14
BP97-04	73°30'02.0"	72°57'00.0"	29	BP97-34	72°25'50.4"	80°24'25.8"	12
BP97-05	73°19'58.0"	72°52'32.0"	29	BP97-35	72°30'31.2"	80°19'43.2"	14
BP97-06	73°10'01.0"	72°53'39.0"	29	BP97-36	72°45'39.6"	80°10'37.8"	17
BP97-07	73°00'01.0"	73°03'55.0"	29	BP97-37	72°58'33.6"	80°04'09.6"	20
BP97-08	72°50'03.0"	73°24'13.0"	26	BP97-38	73°12'51.0"	80°00'19.2"	31
BP97-09	72°39'55.0"	73°46'19.0"	21	BP97-39	73°32'09.6"	79°55'03.0"	40
BP97-10	72°30'10.0"	74°04'51.0"	15	BP97-40	73°40'51.0"	80°36'39.0"	37
BP97-11	72°20'07.0"	74°09'42.0"	13	BP97-41	73°41'53.4"	80°46'22.2"	39
BP97-12	72°10'13.0"	74°17'37.0"	13	BP97-42	73°53'57.6"	81°40'01.2"	32
BP97-13	72°35'01.8"	73°45'13.2"	18	BP97-43	73°42'33.0"	82°48'48.0"	31
BP97-14	72°35'54.6"	73°54'34.8"	18	BP97-44	74°00'00.0"	79°25'49.2"	30
BP97-15	72°38'20.4"	73°49'56.4"	19	BP97-45	73°59'55.8"	77°30'14.4"	24
BP97-16	72°45'04.8"	73°29'36.6"	24	BP97-46	73°59'57.6"	77°12'14.4"	27
BP97-17	72°41'19.2"	73°43'50.4"	20	BP97-47	72°35'00.6"	73°44'54.6"	18
BP97-18	73°57'42.0"	76°08'19.8"	25	BP97-48	72°57'40.8"	73°08'51.6"	29
BP97-19	74°00'02.4"	79°01'28.4"	30	BP97-49	73°12'34.2"	72°53'40.8"	29
BP97-20	73°59'48.0"	79°25'34.8"	30	BP97-50	73°36'39.6"	72°57'04.8"	28
BP97-21	74°00'02.4"	81°00'27.6"	41	BP97-51	73°53'17.4"	73°10'19.8"	30
BP97-22	73°50'10.8"	80°36'46.8"	37	BP97-52	74°00'01.2"	72°39'43.2"	30
BP97-23	73°41'22.8"	80°16'23.4"	38	BP97-53	73°37'35.4"	74°51'49.2"	21
BP97-24	73°32'04.2"	79°55'16.2"	40	BP97-54	73°19'51.0"	75°20'36.6"	15
BP97-25	73°20'00.0"	79°57'44.4"	31	BP97-55	73°13'27.9"	75°37'08.4"	14
BP97-26	73°07'06.0"	80°02'19.2"	25	BP97-56	72°53'23.4"	75°28'57.0"	14
BP97-27	72°53'21.0"	80°05'33.0"	19	BP97-57	73°02'39.6"	75°35'15.6"	14
BP97-28	72°49'56.4"	80°09'59.4"	19	BP97-58	73°39'01,2"	74°50'19.2"	23
BP97-29	72°41'43.8"	80°12'00.6"	16	BP97-59	73°49'23.4"	74°43'45.6"	18
BP97-30	72°30'30.6"	80°20'10.8"	14				

OCEANOGRAPHY

AND

HYDROCHEMISTRY

VARIABILITY OF WATER TEMPERATURE, CONCENTRATION OF DISSOLVED OXYGEN, ALKALINITY AND SILICON IN THE VEGA STRAIT (KARA SEA)

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Abstract

Measurements of water temperature, dissolved oxygen, alkalinity and silicon at the polar station Dikson in the Vega Strait were analysed for their seasonal variability. These measurements were carried out at discrete intervals of ten days for the period from 1978 to 1986. The amplitudes of the seasonal variability of water temperature and hydrochemical parameters, periods of extremes and their duration are determined. The asynchronity of the seasonal extremes of various parameters of the sea water is noted and interpreted to be caused by the incongruity of hydrological and biochemical cycles.

Introduction

Information about the seasonal and interannual variability of hydrophysical and hydrochemical parameters obtained at coastal stations over long periods are important for understanding the regime of the Kara Sea system. Until the present time scientific investigations on the variability of hydrophysical and hydrochemical parameters in the Kara Sea were based only on summer (July - October) and winter (March - May) measurements (Rusanov and Vasiljev, 1976; Rusanov et al., 1979; Pavlov et al., 1996). The year round measurements in the Vega Strait enable 1) to determine the main phases of the seasonal variability of hydrochemical parameters, 2) to investigate the features of their intra- and interannual variability, 3) to estimate amplitudes of oscillations and 4) to reveal the factors influencing seasonal and interannual variability in more details.

The Vega Strait is located in the southeastern part of the Kara Sea between Dikson Island and the Taymyr Peninsula to the north of Yenisei Gulf (Fig. 1). The mean depth of the strait is about 10 m, and the maximum depth (in a ship channel) - up to 24 m.

Several investigators pointed out that this region is strongly influenced by the River Yenisei (for example, Antonov, 1946, 1963; Ivanov et al., 1984; Burenkov and Vasilkov, 1994; Pavlov et al., 1996). Mean annual water discharge of River Yenisei (p.Igarka) is about 18200 m^3/s (574 km^3/year). The main portion of the river run-off is transported during the flood period in spring-summer and in fall, that is, 78% of the total run-off volume is in May-September. Maximum discharge near Igarka is up to 154000 m^3/s. In wintertime the river run-off is minimum (mean values are 5000-6000 m^3/s). During wintertime the Yenisei Gulf and Vega Strait are covered by fast ice having a thickness of up to 1.5-2 m.

The main goal of this paper is to characterize and describe regular features in the variability of water temperature and hydrochemical parameters in the Vega Strait in the surface (depth level 0 to 5 m) and in the bottom (depth levels 10 or 11 m) layers.

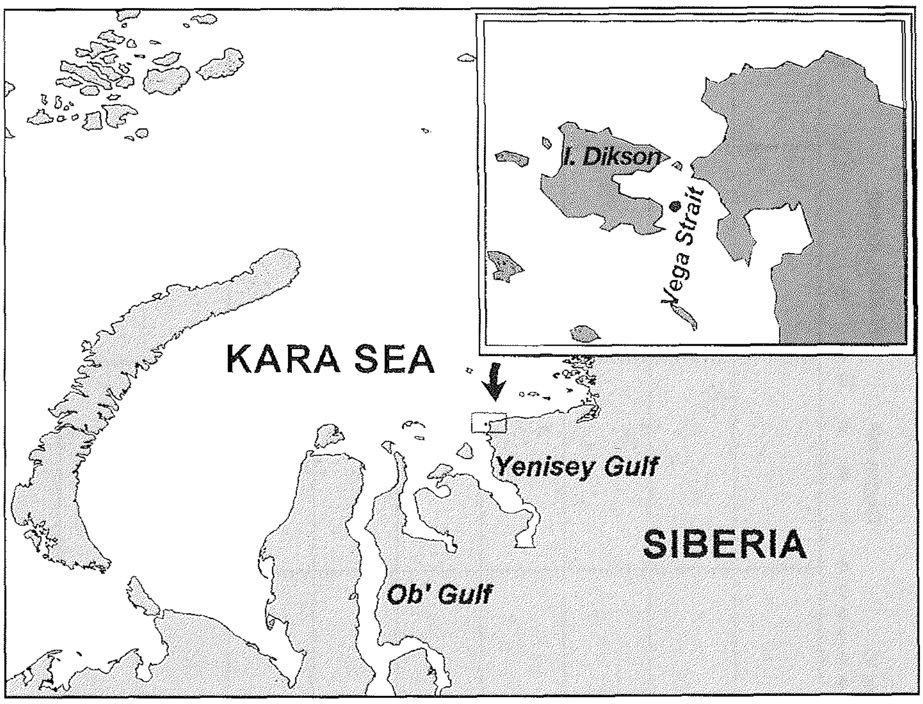

Fig. 1. Location of the Vega Strait in the southeastern Kara Sea. The hydrographical station is indicated by a dot in the inserted map.

Data and methods

In this paper the observations carried out by the employees of the polar station Dikson in the Vega Strait (73° 28' N, 80° 29' E) during the period from 1978 till 1986 are presented. The measurements were carried out, as a rule, every ten days by using standard techniques (Oradovsky, 1977). Accuracy of the water temperature measurements is 0.01 °C, errors in the determination of the hydrochemical parameters are: dissolved oxygen - less than 0.05 ml/l, alkalinity - less than 0.01 mg-eq/l and dissolved inorganic silicon - less than 10 %.

Results

In Figures 2 and 3 the measurements at the surface and bottom (10-11 m) layers in the Vega Strait are presented. The mean monthly discharge of the River Yenisei for the period considered is also presented in Figure 2.

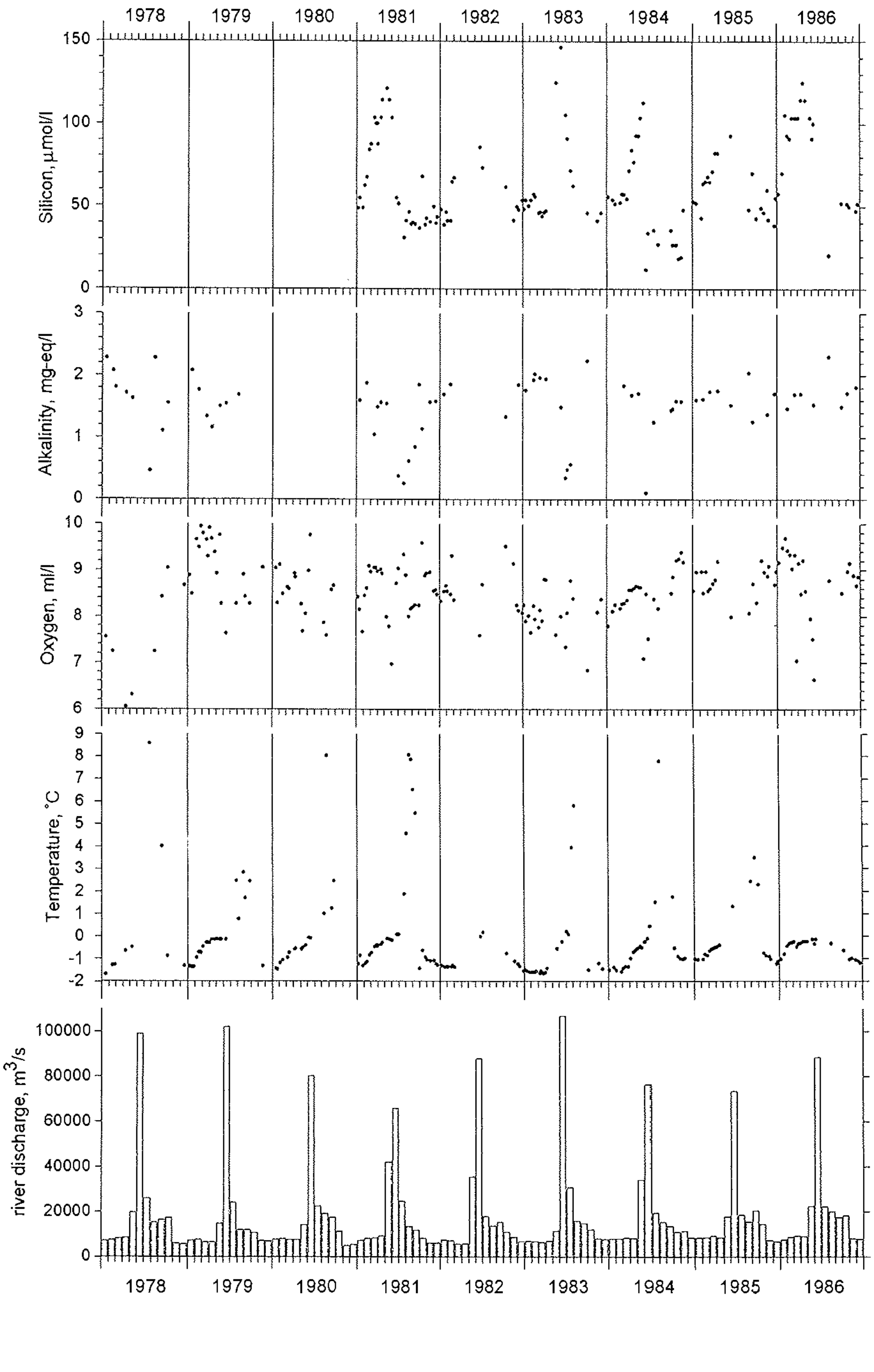

Fig. 2: Hydrographical and hydrochemical parameters at the water surface in the Vega Strait and mean monthly discharge of the Yenisei River from 1978 to 1986.

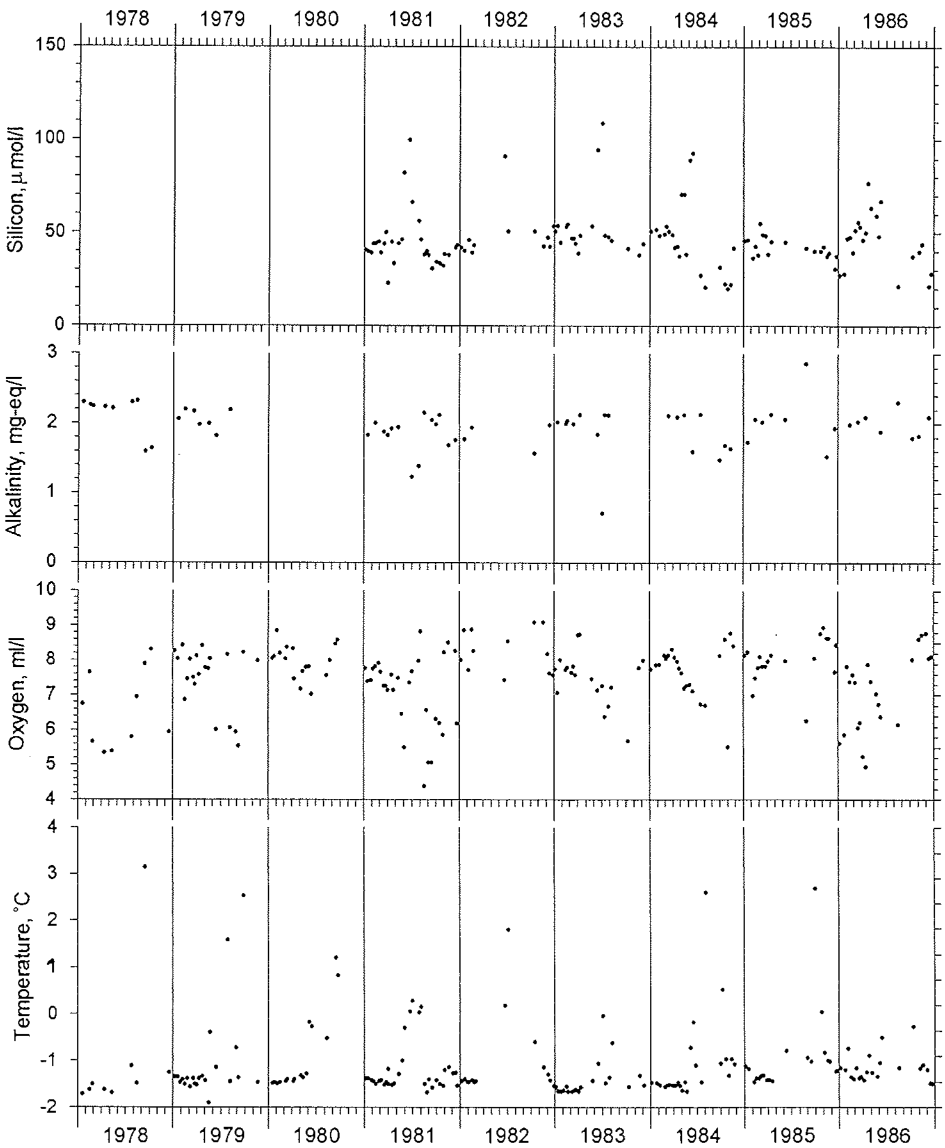

Fig. 3: Hydrographical and hydrochemical parameters in the bottom layer in the Vega Strait in 1978-1986.

The water temperature and the hydrochemical parameters for the period of observations varied widely within a precisely expressed annual cycle. The phases of annual cycles of various parameters of the sea water do not coincide. Pair correlation coefficients between different parameters are very low. The correlation coefficients with river discharge are somewhat higher, but still quite low. Thus, the correlation coefficients between the river discharge and water temperature in the Vega Strait is only 0.47 or shifted by 2 months, the river discharge - concentration of silicon is 0.51 and the river discharge - concentration of oxygen is only 0.33 with a shift of 2 months.

The amplitude of the water temperature variations in the annual cycle in the surface layer (depths 0 and 5 m) exceeds 10 °C and in the bottom layer - 5 °C. Minimum temperature was observed in January - February. In the surface layer it ranged from -1.65 up to -1.70 °C in different years, and in the bottom layer water temperature reached values of -1.90 °C. Maximum temperature in the surface layer was usually observed in August and reached 8.58 °C.

The concentration of oxygen in the surface layer varied from 5.61 up to 9.94 ml/l. As a rule, the minimum values in the annual cycle were measured in the winter period, but for particular years low values of oxygen were also observed in autumn. The maximum values of oxygen occur typically at the end of winter (March - April) and beginning of spring (May). In the bottom layer the amplitude of the variation of oxygen concentration exceeded 5 ml/l.

The alkalinity in the surface layer varied during the investigation period from 0.10 up to 2.30 mg-eq/l and in the bottom layer it varied from 0.70 up to 2.42 mg-eq/l. The minimum values were observed in June - July and maximum values were observed in winter months.

The concentration of silicon varied in the annual cycle in the surface layer from 11 up to 146 mmol/l and in the bottom layer it ranged from 20 up to 110 mmol/l. The minimum values were observed, usually, from August until December. However, sometimes (for example in 1984) the minimum of the silicon concentration was observed in June. The maximum values of silicon are typically reached in May - June.

The temporal variability of water temperature, concentrations of oxygen and silicon for one of the years (1981) with most measurements is presented in Figure 4.

Discussion

It is possible to explain the asynchronity of the seasonal extremes of water temperature, oxygen, alkalinity and silicon by analyzing the main factors influencing the seasonal variability of the hydrological and hydrochemical parameters.

The annual variability of water temperature in the Vega Strait is caused by river water advection from the south and heat exchange with the atmosphere. Short-term increase of the water temperature in August up to 7-8 °C is mainly caused by solar radiation and influence of warm river water penetrating from the Yenisei Gulf.

The solubility of oxygen in sea water is inversely related to water temperature and salinity. The annual variability of oxygen concentrations should correspond to variations of water temperature but in the surface layer the increase of oxygen in spring and summer is related to the development of phytoplankton

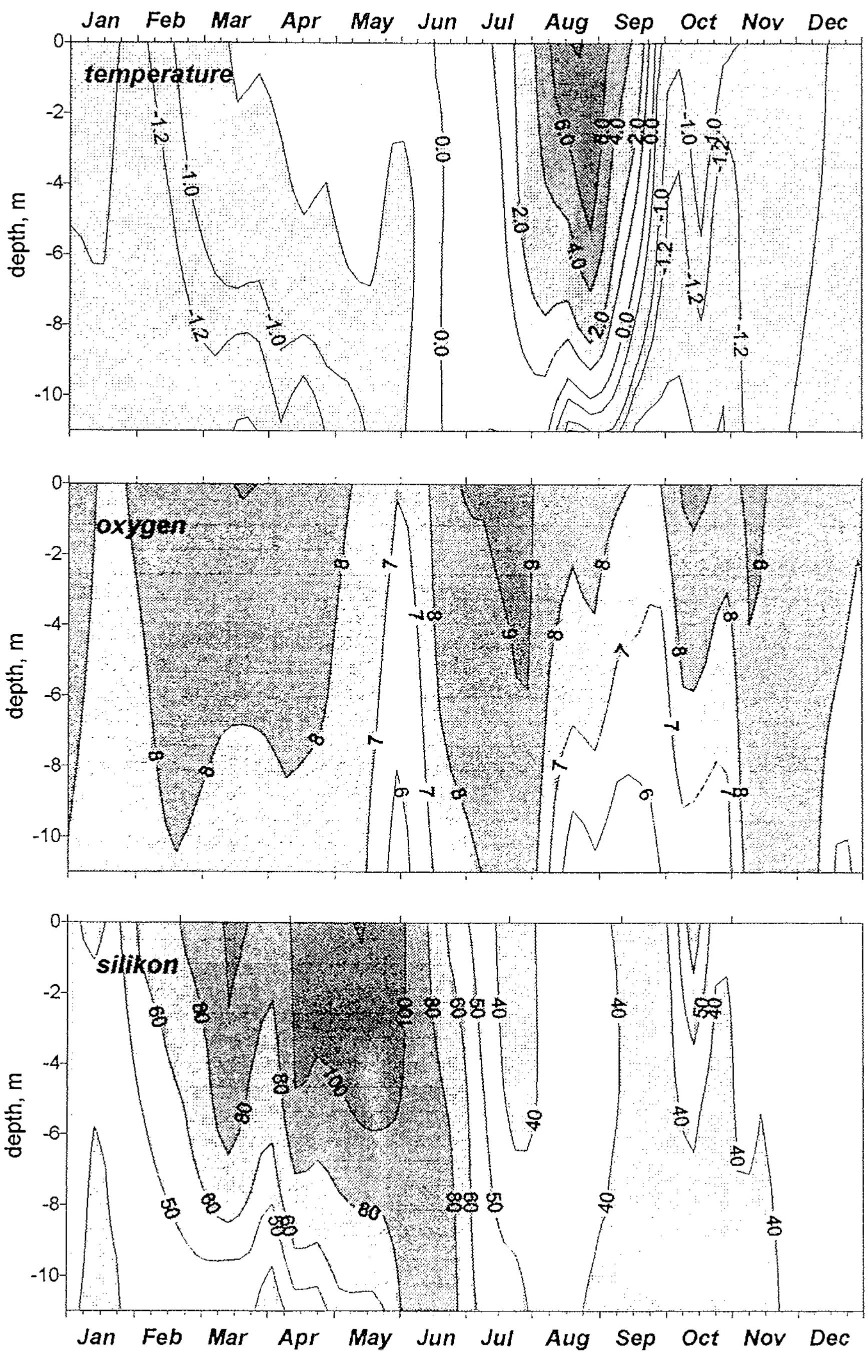

Fig. 4: Temporal variability of water temperature, dissolved oxygen and silicon in the Vega Strait in 1981.

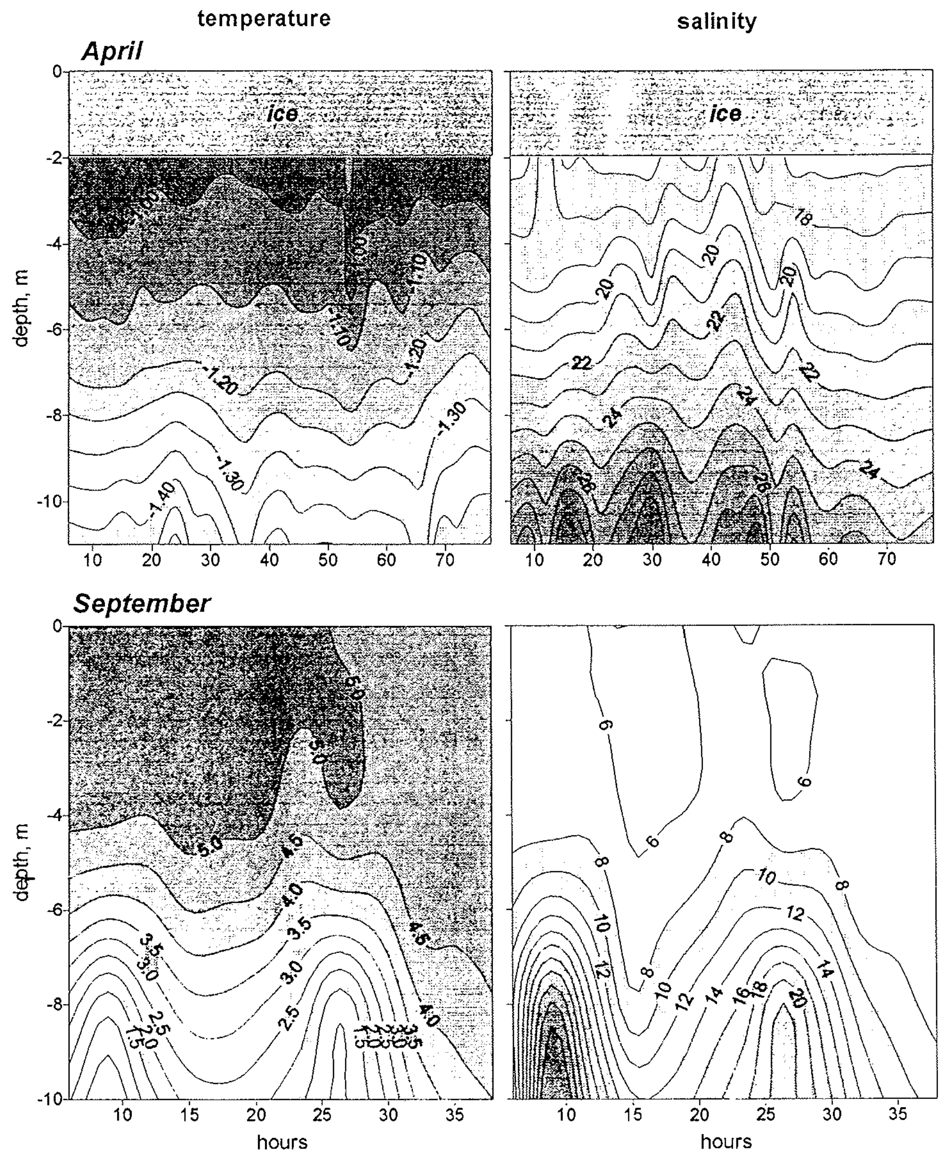

Fig. 5: Variability of water temperature and salinity at the multi-hour CTD station in the Vega Strait in winter and summertime.

(Usachev, 1968) producing oxygen during photosynthesis. In the bottom layer the oxygen is spent for oxidation of organic and mineral substances, both of local origin and transported by river waters. Therefore, maximum values of oxygen in the surface layer were observed in the spring months when the water temperature was quite low yet and light conditions were already sufficient for phytoplankton blooms. With increase of water temperature and river run-off oxygen concentrations in the surface layer decreased appreciably.

The alkalinity and silicon concentrations are indicators of river run-off (Shpaikher and Rusanov, 1972; Rusanov et al., 1979; Stunzhas, 1995). These parameters are also dependent on the biological processes. The maximum silicon concentrations are observed in the Vega Strait during the Yenisei River flood period in spring. In river water the silicon concentration is not constant and varies considerably during the year. The highest values of silicon are typical for winter months prior to the spring river flood. Therefore the silicon maximum in the seasonal cycle is displaced relatively to the maximum of water temperature and maximum of river run-off (minimum of alkalinity). Apparently, the sharp decrease of silicon concentrations in the summer months in the Vega Strait is also related to the biological consumption by diatoms.

Against this background of seasonal and interannual variability of hydrological and hydrochemical parameters there is also the variability of synoptical and tidal temporary scales caused by intensive dynamic processes (surges, tides and internal waves) (Gribanov et al., 1997). The small depths and well pronounced stratification in the Vega Strait and Yenisei Gulf enhance the influence of these dynamic processes on the spatial and temporal variability of water temperature and salinity both in summer and wintertime under the fast ice cover (Fig. 5).

In wintertime water temperature variations can reach values of 0.3 °C in the surface layer and up to 1.0 °C at the bottom within a few hours. Variations of water salinity are - up to 0.3 and 2-3, respectively. In summertime the processes are more intensive and temperature variations reach 0.5 °C at the water surface (also influenced by daily variations of air temperature) and at the bottom up to 3-4 °C within a few hours and variations of the water salinity are 0.6 and up to 10-15, respectively.

Unfortunately, measurements of hydrochemical parameters at discrete intervals of 3-6 hours were not executed, but obviously dynamic processes on synoptical and tidal scales contribute to the total variability of these parameters.

The multiple complex hydrological and biochemical processes, differently effecting the distribution of hydrochemical parameters, determines the temporary variability of the sea environment in the Vega Strait.

Conclusions

Hydrographic measurements in the coastal zone of the Kara Sea are carried out on one, at the best, two expeditions per summer. It is important to determine the temporal scale of the data in the annual cycle of variability of sea water parameters. Results of regular measurements at coastal stations, including observations in the Vega Strait, allow us to determine the period of the annual cycle when the observations on expedition were carried out, and to calibrate these observations.

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MICRO- AND MESOSCALE OSCILLATIONS OF THERMOHALINE CHARACTERISTICS IN THE COASTAL ZONE IN THE VICINITY OF THE YENISEI GULF

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Abstract

On the basis of results of the joint Russian-German expedition 1997 onboard RV "Akademik Boris Petrov" in the Kara Sea and also of available data for previous years micro- and mesoscale oscillations of the thermohaline characteristics in the coastal zone in the vicinity of the Yenisei Gulf to the north off polar station Dikson are investigated.

Introduction

The variability of the thermohaline characteristics in the pycnocline is most important for understanding the hydrophysical processes in the vicinity of river mouths, where there is an interaction of fresh river and saline marine waters, and in the coastal zone of the sea on the whole (Gribanov et al., 1997).

Internal waves are closely linked with the variability of the thermohaline structure. Instability and destruction of the internal waves on the shelf and in the coastal zone results in formation of vortical zones, leading to more intensive mixing of water masses and amplification of the turbulent diffusion of heat and salt.

The analysis of measurements on daily and multi-daily CTD stations in the coastal zone of the Kara Sea (the measurements were done by traditional methods at discrete intervals of 1 hour and more) has shown the presence of internal waves with tidal and subtidal (3-8 hours) periods (Gribanov et al., 1997; Stanovoy, 1984, 1997; Pavlov et al., 1996). Within the framework of the Russian-Swedish expedition "Tundra-94" in the southwestern part of the Kara Sea water temperature oscillations in the pycnocline were measured during about 1 hour (at discrete intervals of 4 seconds). The analysis of these measurements has shown the presence of short-period internal waves with periods 10-12 and 2-3 minutes (Zakharchuk and Presnyakova, 1997).

The observations obtained within the framework of the joint Russian-German expedition 1997 onboard of RV "Akademik Boris Petrov" enable to analyse series of observed oscillations of the thermohaline parameters measured at one station to the north of Dikson Island in different years at variable discrete time intervals, and to supplement spectra of internal waves in the short-period part of spectra.

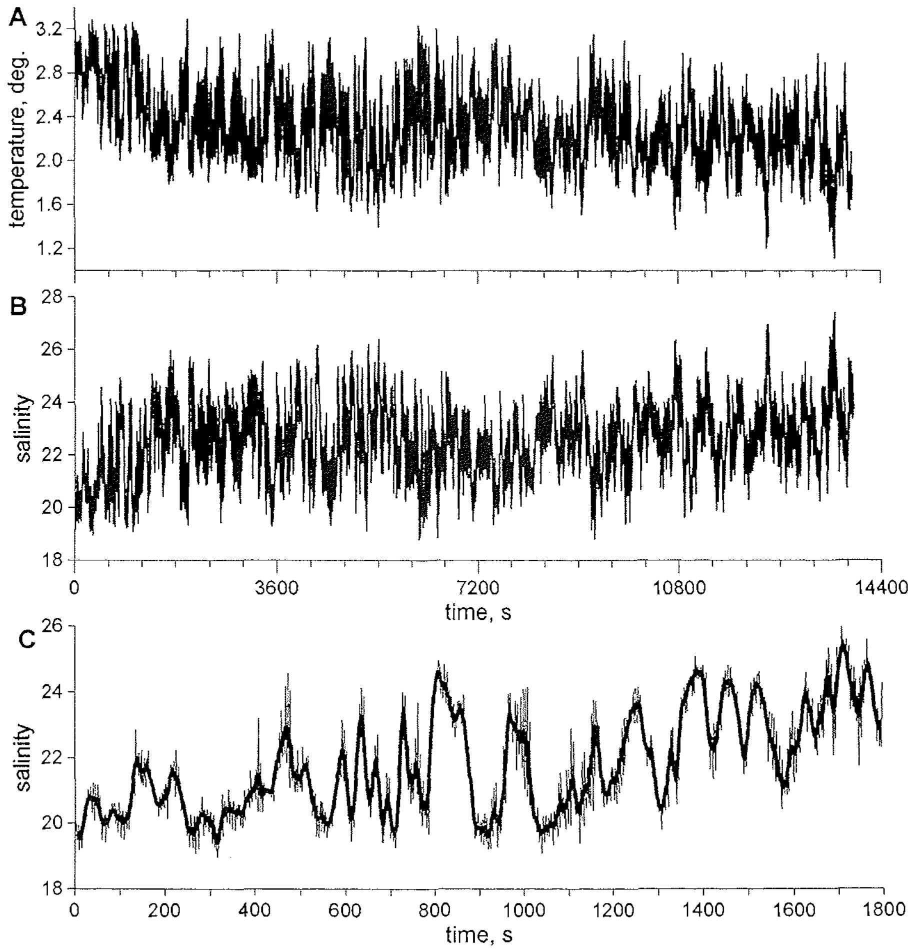

Fig. 1. Raw data of oscillations of water temperature (A) and salinity (B) at the depth 12.25 m and the filtered salinity oscillations (C).

Data

Oceanographic measurements during the joint Russian-German expedition on RV "Akademik Boris Petrov" in September 1997 to the Kara Sea were carried out with the hydrophysical CTD Set OTS-116 Probe Series 3 produced by Meerestechnik Electronic GmbH, Germany (Churun and Ivanov, 1998). This probe allows to record water pressure, temperature, conductivity and dissolved oxygen content in sea water in the regime of sounding (the vertical interval of parameters recorded is set) or exposition on the desired depth (the time interval of registration is set). The sensors of the CTD probe were checked before the expedition at Meerestechnik Elektronik.

The measurements of temporary variability of water temperature, conductivity (salinity) and dissolved oxygen were executed from anchored vessel at the standard station not far from Dikson Island (74° 00' N, 80° 00' E). The hydrological parameters were recorded in this region first at discrete intervals of 1 second during almost 4 hours (13919 data points). A CTD cast was carried out before the beginning of the long-term measurements. The results of sounding were used to determine the depth of the pycnocline layer, allowing to place the CTD set in the pycnocline layer (mean depth was 12.25 m). After the end of measurements the CTD cast was repeated.

The depth of sensors varied from 11 to 13 m because the CTD probe was deployed from the vessel. We assume, that water temperature and salinity are a linear superposition of oscillations caused by vertical displacements of sensors and by internal waves. Using the recorded depth of the sensors and averaged data of CTD soundings before and after the long-term measurements, the oscillations caused by vertical displacements of sensors were filtered. As a result the oscillations of water temperature and salinity on depth 12.25 m were obtained (Fig. 1a,b). The minimum periods of free internal waves should be more than the maximum of the Brunt-Väisälä period, which in our case reaches 20 seconds. Therefore the data rows were smoothed by a method of running averaging (Fig. 1c). All oscillations with period less than 20 seconds are referred to turbulent pulsings.

For comparative analysis previous measurements from the same station were taken. In summer 1963 temperature oscillations were measured in the pycnocline layer at 10 m depth at discrete intervals of 1 hour (427 data points) by photothermograph. A mooring with an OTS-1500 probe on two levels was deployed within the framework of the joint Russian-Norwegian expedition in summer 1994 also at this station (Zhukov et al., 1997). The hydrological parameters were recorded in the pycnocline layer at the depth 10.5 m at discrete intervals of 10 minutes (2527 data points).

Results and discussion

The vertical distribution of water temperature, salinity and Brunt-Väisälä frequency at the station for all three years are presented in Figure 2. In summer 1963 the measurements were done on discrete horizons, and in 1994 and 1997 the soundings were made on one depth. A very strong thermocline and halocline occurred in a thin layer in the depth interval 9-15 m, thus gradients of water temperature are on the average 0.6-0.8 °C/ m with maximum values up to 0.15 °C / 10 cm, and salinity gradients are 2-2.5 ‰ / m and 1 ‰ / 10 cm, respectively (Fig. 2). The location of sensors is marked on the diagrams by solid points.

In Figure 3 the spectra of water temperature and salinity oscillations for all three series (in 1963 - only temperature) are presented. The observations of 1997 provide a high-frequency part of the spectrum.

The spectra of water temperature and salinity oscillations are quite similar. The level of spectral density falls within an increase of frequency in accordance with the degree "-2" in an interval from inertial frequency up to 1 cph and with the degree "-3" in high-frequencies. The spectra have a continuous disposition, showing the presence of a set of internal waves with casual phases and amplitudes. The main pronounced periods of oscillations are marked (Fig. 3). Inertial frequency f (in this region it is close to semi-durnal tidal frequency) and maximum Brunt- Väisälä frequency N are marked also in Figure 3.

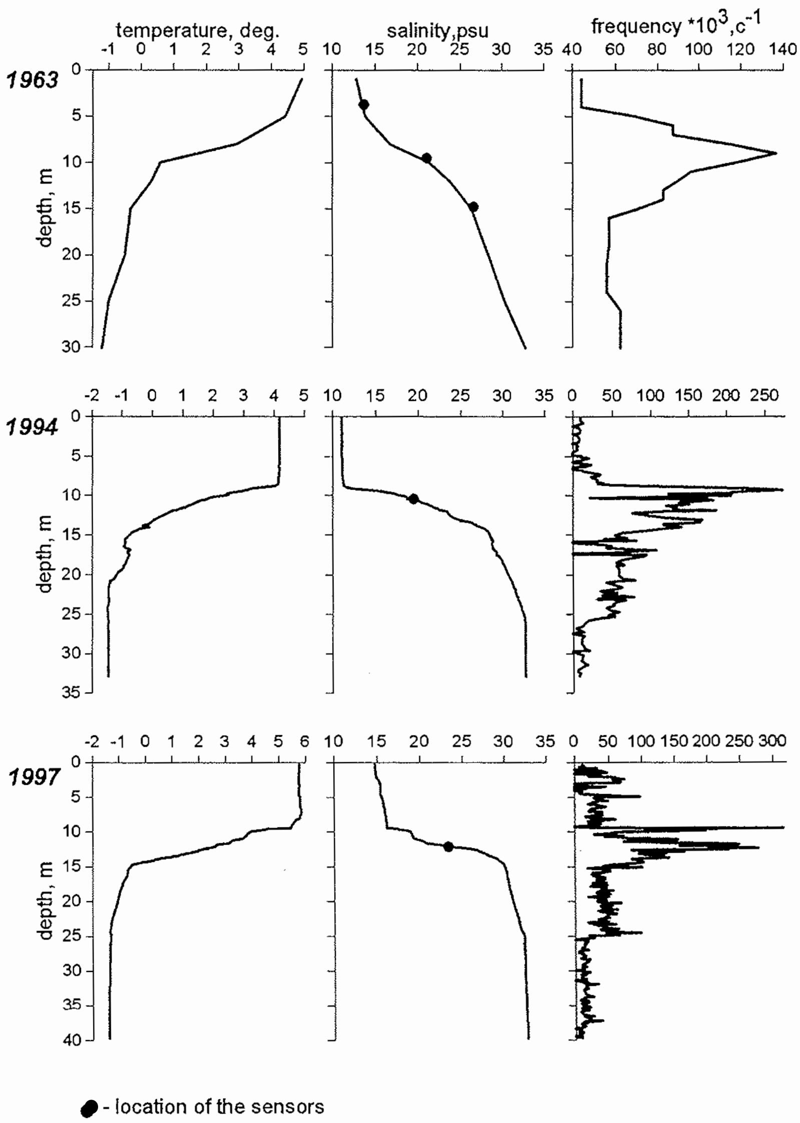

Fig. 2. Vertical distribution of the water temperature, salinity and Brunt-Väisälä frequency at the standard station for all three years.

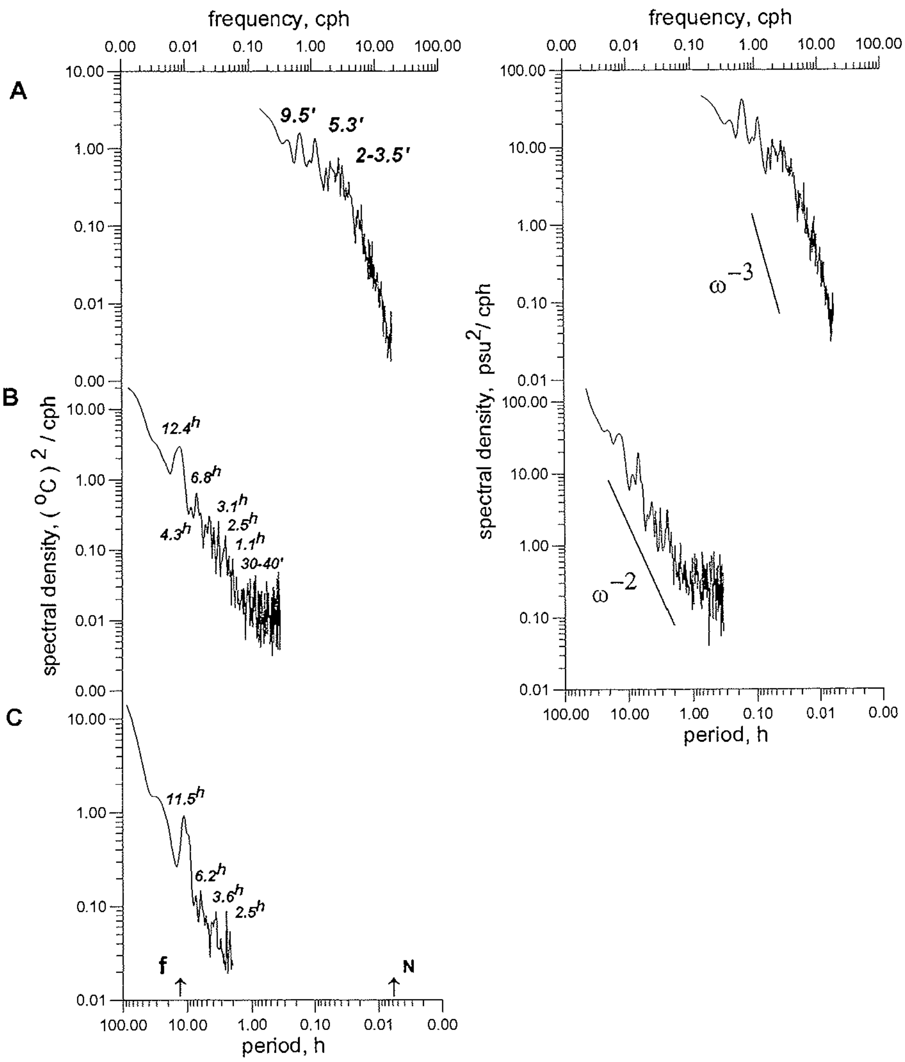

Fig. 3. Spectra of water temperature and salinity oscillations for all three series of measurements: 1997 (A), 1994 (B) and 1963 (C) years. Inertial frequency f and maximum Brunt-Väisälä frequency N are marked.

The oscillations with tidal periods (about 12 hours) and with subtidal-shallow (about 6, 4 and 3 hours) periods are well demonstrated. The presence of internal waves with such periods in the coastal zone of the Kara Sea already was mentioned earlier (Gribanov et al., 1997; Stanovoy, 1984,1997). Some shifts of frequency (for example, the period 11.3 hours in the Fig. 3b) are due to intensive water dynamic in this area (Doppler's effect).

The oscillations with periods from 2.5 hours till 30-40 minutes are arranged in packets with a periodicity of about 12 hours. It is necessary to note the sharp amplification of amplitudes of the oscillations in packets with a periodicity of 3-5 day which are caused, obviously, by synoptical (storm surges) phenomena.

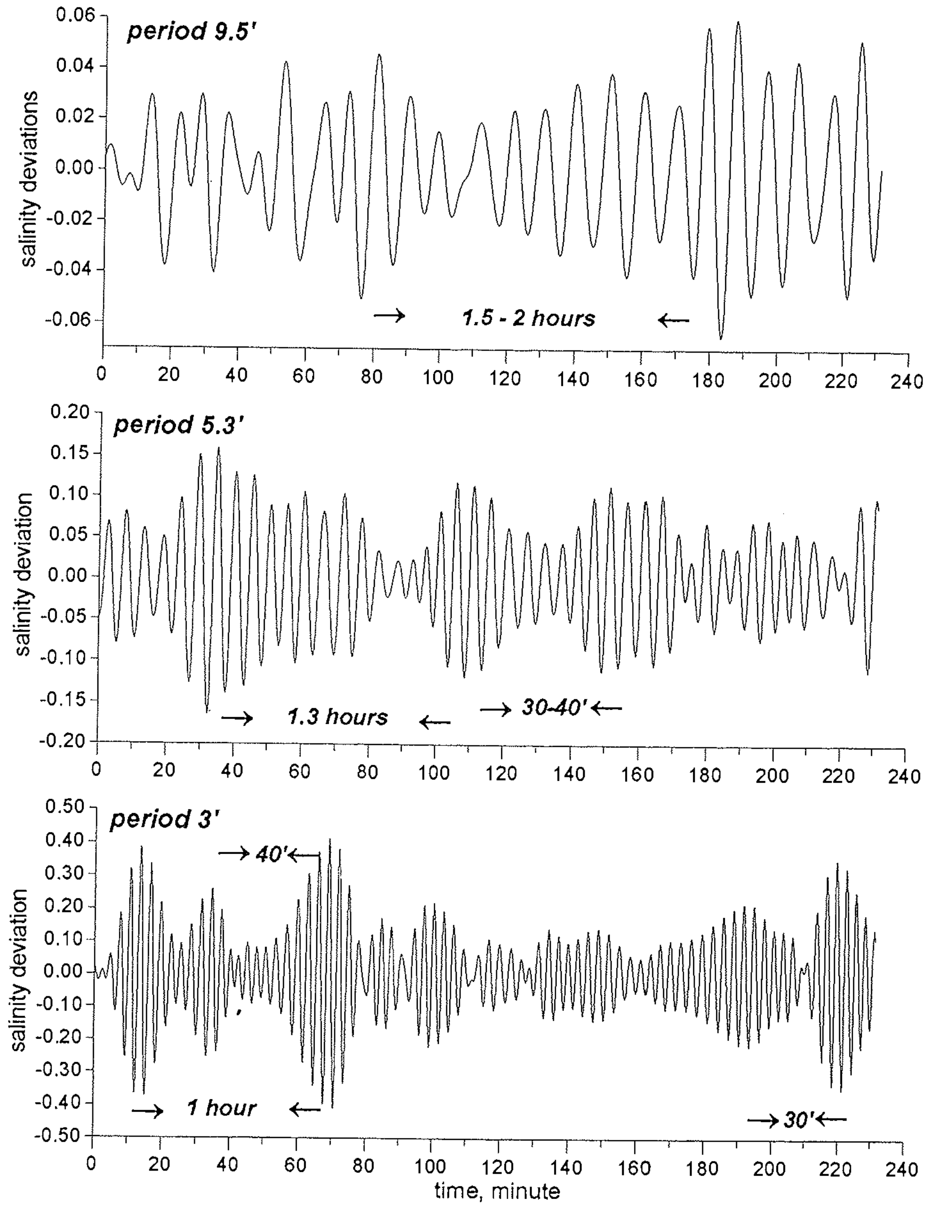

Fig. 4. High-frequency oscillations of the water salinity obtained with the strip-selected filter.

The short-period part of the spectrum added due to observations in 1997 supplements a set of main periods of internal waves by well expressed periods 9.5, 5.3 and 2-3.5 minutes (Fig. 3a). The oscillations of the water salinity within these periods obtained by the strip-selected filter are presented in Figure 4. The arrangement in packets of short-period waves is well pronounced, thus the packets have periods from 30 minutes till 2 hours. Let us note also, that oscillations with a period of 3 minutes are most intensive. The amplitude of water salinity oscillations with this period reaches values up to 0.8-0.9, while amplitudes of oscillations with a period of 9.5 minutes reach values 0.10-0.12.

The approximate estimation of amplitudes of internal waves for all three series of observations at average water temperature and salinity gradients is about 1.5 - 2.0 m.

Thus, it is demonstrated, that the dynamic instability and destruction of internal waves in a shallow coastal zone results in the cascade process of swapping of energy from internal waves having tidal period to high-frequency waves and, in total, to turbulence and formation of the fine thermohaline structure (Fig. 2c). There is, also, the quite realistic possibility of energy transfer from wind waves to high-frequency internal waves owing to resonant effects at the shallow depth of the pycnocline.

Conclusions

The analysis of measurements obtained in September 1997 within the framework of the joint Russian-German expedition onboard of the RV "Akademik Boris Petrov" has allowed to expand our knowledge about high-frequency oscillations of the thermohaline parameters in the pycnocline layer.

As a result of the analysis of obtained data it was possible to reveal presence of internal waves with periods 9.5, 5.5 and 2-3.5 minutes in the region to the north off Dikson Island. This is in good agreement with results obtained for the southwest part of the Kara Sea in 1994 (Zakharchuk and Presnyakova, 1997).

The dynamic instability and destruction of internal waves in a shallow coastal zone results in the cascade process of swapping of energy from internal waves having tidal period to high-frequency waves and, in total, to turbulence and formation of the fine thermohaline structure.

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MARINE BIOLOGY

The significance of biological processes for the transformation of matter in estuaries is well documented for boreal and tropical regions of the world ocean. Estuaries of Arctic rivers represent very dynamic environments and are characterised by strong seasonal changes. However, there is virtually nothing known about the relevance of this seasonality and the biological processes themselves concerning transport and modification of fluvial matter in polar regions. The strongly seasonal river run-off in the Eurasian Arctic implies that an enormous amount of organic and anorganic substances enters and moves during a relatively short period of the year up to the external areas of the estuaries and further north. Beside the variable light conditions and seasonal ice cover this pulse of fluvial matter and heat will affect biological processes und transformation rates at large geographical scales. The relation between pelagic and benthic processes in polar waters was summarised by Grebmeier and Barry (1991). They found a direct influence of the input of organic material on the abundance and biomass of benthic communities, which reflects the variability of the hydrography, sea ice cover, light supply, and pelagic food web structure.

Our biological studies focuses on key species in order gain better knowledge about their population dynamics, reproduction biology, eco-physiology and feeding ecology. Based on these information we will be able to evaluate the importance of the biosphere for the fate of the spreading material originating from large Siberian rivers on its way into the central Arctic Ocean.

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DISTRIBUTION OF PHYTOPLANKTON BIOMASS AND NUTRIENT CONCENTRATIONS

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Arctic river estuaries are very dynamic environments for phytoplankton development mainly due to the strong input of river water causing vast brackish water areas. The largest Siberian rivers drain into the Kara Sea. The inorganic nutrients are one of the main parameter needed for biological and physical investigations. In addition, the phosphate and silicate contents can be used as a tracer for identifying different water masses. These data are not only important to understand the processes of the Kara Sea, they are also important to understand the interaction with the Central Arctic Ocean. The aim of this study was to investigate the horizontal and vertical distribution of phytoplankton biomass with regard to the different physical and chemical conditions. Furthermore, together with the results from investigations of the other groups a more complete picture of the pathway of primary produced carbon could be established in the future.

During the expedition to the Kara Sea with RV 'Akademik Boris Petrov' in 1997 inorganic nutrients and chlorophyll a were measured. Nutrient concentrations ranged from 0 - 2.02 for nitrate, 0.13 - 0.67 for phosphate, 25 - 76.5 for silicate, and 0.12 - 3.01 for ammonium. Nitrate, phosphate and ammonium were slightly lower, and silicate was slightly higher in the area influenced by the Yenisei. In general, lower nitrate, phosphate, ammonium and higher silicate values correspond with higher chlorophyll a concentrations. Chlorophyll a ranged from 0.73 to 3.13 µg/L in the surface layers; somewhat higher phytoplankton biomass was found in the middle and eastern parts of the investigation area. Except for some stations, surface chlorophyll a concentrations showed an inverse relationship with surface salinity. For nitrate and other nutrients this relationship had a lower correlation coefficient.

Material and Methods

Water samples to estimate inorganic nutrients and phytoplankton biomass were collected with a Niskin Rosette sampling system.

Inorganic nutrients

During the cruise 25 surface samples were taken for further laboratory analyses at the AWI. All samples were poisoned with mercuric chloride. At the AWI the concentration of nitrate, nitrite, ammonium, phosphate and silicate were determined using a Technicon Autoanalyser II (Bran and Lübbe) essentially according to standard methods: nitrate and nitrite based on the method of Armstrong et al. (1967), ammonium on Koroleff (1969), phosphate on Eberlein and Kattner (1987), and silicate on Grasshoff et al. (1983). For accuracy duplicate samples were analysed for each determination with four standards at the beginning and two standards at the end of the run.

Table 1: Inorganic nutrient concentrations (μM) of nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+), silic acid Si $(OH)_4^-$, and phosphate (PO_4^{2-}) in the surface waters during the Kara Sea expedition 1997 with RV "Akademik Boris Petrov".

Station	NO_3^-	NO_2^-	NH_4^+	Si $(OH)_4^-$	PO_4^{2-}
1	0.05	0.01	0.12	59.83	0.19
10	1.09	0.07	1.38	24.97	0.50
12	1.31	0.08	2.03	26.43	0.61
17	2.02	0.11	3.01	29.82	0.67
18	0.05	0.01	0.24	54.89	0.26
21	0.04	0.02	0.66	44.27	0.16
24	0.00	0.01	0.31	55.01	0.13
27	0.26	0.03	0.36	60.03	0.22
30	0.22	0.03	0.23	66.64	0.31
32	0.14	0.03	0.18	76.47	0.34
34	0.17	0.03	0.34	73.76	0.25
35	0.19	0.01	0.48	74.34	0.44
40	0.24	0.03	0.32	53.43	0.27
41	0.10	0.02	0.22	50.76	0.20
42	0.07	0.03	0.41	41.99	0.20
43	0.26	0.03	0.37	49.16	0.21
46	0.06	0.02	0.21	48.86	0.17
47	1.44	0.08	0.52	33.31	0.53
48	1.28	0.07	0.52	27.40	0.40
49	0.60	0.05	0.33	34.20	0.41
50	0.32	0.03	0.42	30.12	0.27
52	0.39	0.04	0.29	32.80	0.27
55	0.83	0.06	0.51	36.26	0.42
56	0.90	0.06	0.33	35.34	0.44
58	1.49	0.09	0.82	33.12	0.45

Phytoplankton

On 21 stations subsamples were taken from 3 to 4 different water depths according to different water masses determined by the CTD profiles. In most cases, samples were taken at the surface, just above and below the pycnocline and close to the bottom. For the chlorophyll a determination 250-500 mL of water were filtered through Whatman GF/F glasfibre filter and stored at -18 °C and analysed at AWI.

The filters were extracted in 90 % acetone and analysed with a spectrophotometer for higher values and with a Turner-Design fluorometer for lower values according to the methods described in Edler (1979). The values from the fluorometer were calibrated with the values obtained with the spectrophotometer.

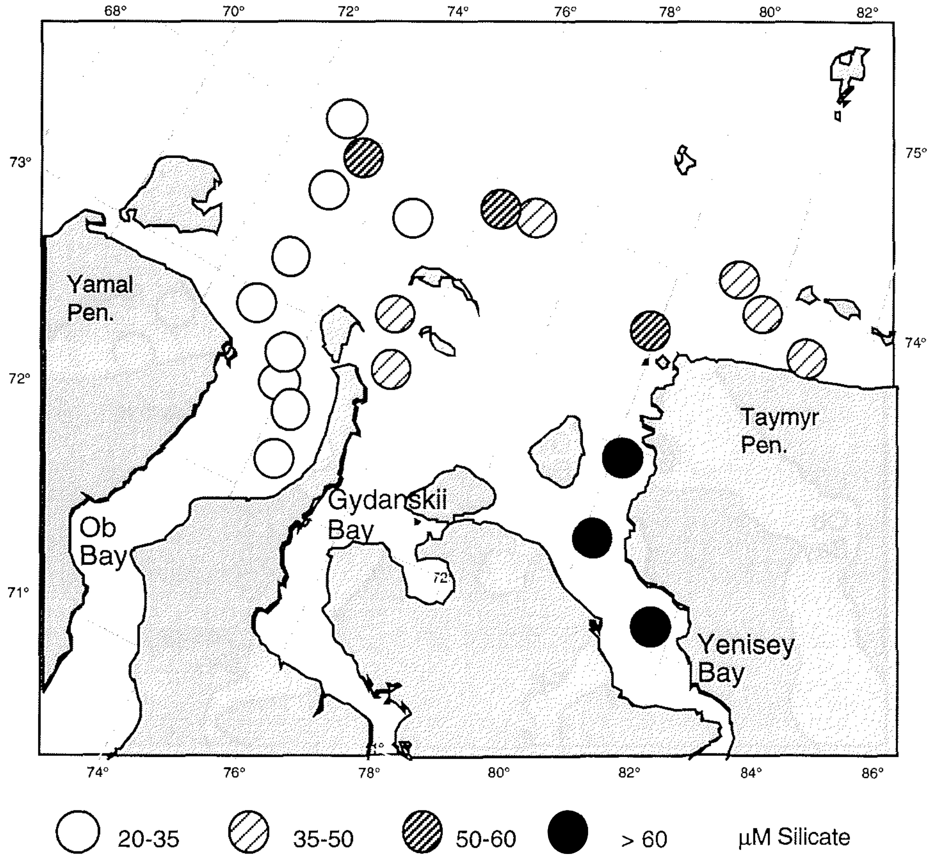

Fig. 1. Silicate concentrations (µM) in the surface waters during the expedition with RV "Akademik Boris Petrov" in 1997.

Results and Discussion

An overview of the location of all stations is given by Matthiessen et al. (this volume). Nutrient concentrations at the surface were relatively low except for silicate. However, there was no large difference in the whole investigation area (Table 1, Figs. 1, 2). At the stations of Ob Bay and Gydanskii Bay nitrate and phosphate concentrations were slightly higher than in the more northern part and in the Yenisei Bay. The opposite was true for silicate. Silicate concentrations could be used as tracers for the different water masses (Fig. 1). Stations influenced by Ob water showed values below 40 µM silicate, whereas stations influenced by Yenisei water showed values above 60 µM silicate. Silicate values at the other stations seemed to be a mixture of both and other water coming in from the north. Similar results have been described by Makkaveev and Stunzhas (1995).

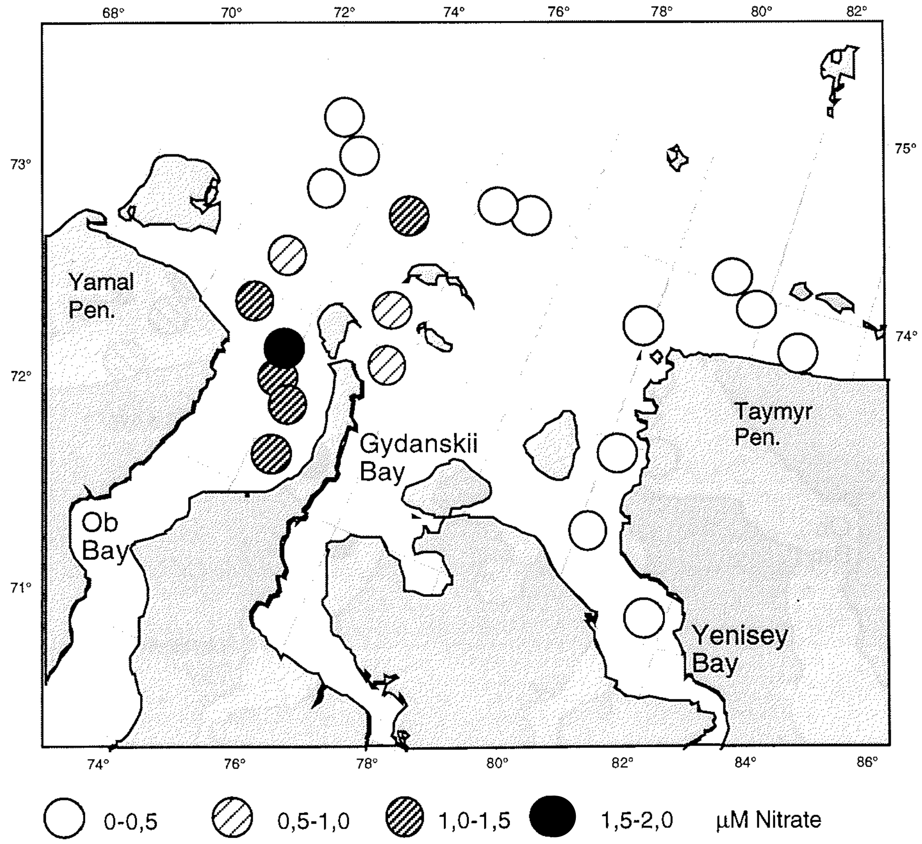

Fig. 2. Nitrate concentrations (μM) in the surface waters during the expedition with RV "Akademik Boris Petrov" in 1997.

Only stations 10, 12, 17 differed somewhat from all other stations. Here, higher ammonium, nitrate, and phosphate concentrations were found. In contrast, the silicate concentrations as well as the chlorophyll a values (Figs. 1, 3; Table 1, 2) were lower than at other stations. We assume that during this first transect in the Ob Bay a different water mass than during the second transect may have prevailed as supported by surface salinities which were much higher during the second transect (Churun and Ivanov, 1998). The high ammonium values could be explained by more heterotrophic activity in this water mass. Grazing is also an explanation for the low phytoplankton biomass found at these stations, although nutrients were still available. Grazers might have developed before phytoplankton was able to utilize all the nutrients.

Table 2. Chlorophyll a - concentrations (Chl a in µg/L) in the water column during the expedition with RV "Akademik Boris Petrov" in September 1997.

Station	Depth (m)	Chl a (µg/L)	Station	Depth (m)	Chl a (µg/L)
1	0	1.60	42	0	1.45
	10.5	0.52		11	0.25
	13	0.46		20	0.21
	17	0.41		28	0.23
	29	0.38	43	0	1.78
10	0	0.73		20	0.56
	10	0.54		28	0.25
	11.5	0.52	46	0	2.25
	13	0.39		10	1.03
12	0	0.73		22	0.48
	7.5	0.71	47	0	1.22
	12	0.57		6	0.57
17	0	0.77		10	0.53
	4.5	0.76		16	0.93
	8.5	0.78	48	0	1.08
	16	0.23		7	0.44
18	0	2.54		11	0.68
	9	2.42		24	0.46
	13	0.48	49	0	1.42
	22	0.55		11	0.32
21	0	1.47		16	0.33
	9	1.00		27	0.31
	14	0.25	50	0	1.26
	35	0.21		9	0.36
24	0	1.96		14	0.63
	12	0.75		26	0.58
	20	0.34	52	0	1.19
	32	0.27		7	0.22
27	0	1.44		10	0.20
	8	0.50		26	0.62
	14	0.39	55	0	3.05
	18	0.50		6	2.89
30	0	3.13		11	2.08
	5	1.29	56	0	2.47
	10	1.16		6	2.39
	12	0.90		12	1.08
32	0	3.11	58	0	1.88
	5	3.12		9	0.52
	8	2.76		15	0.49

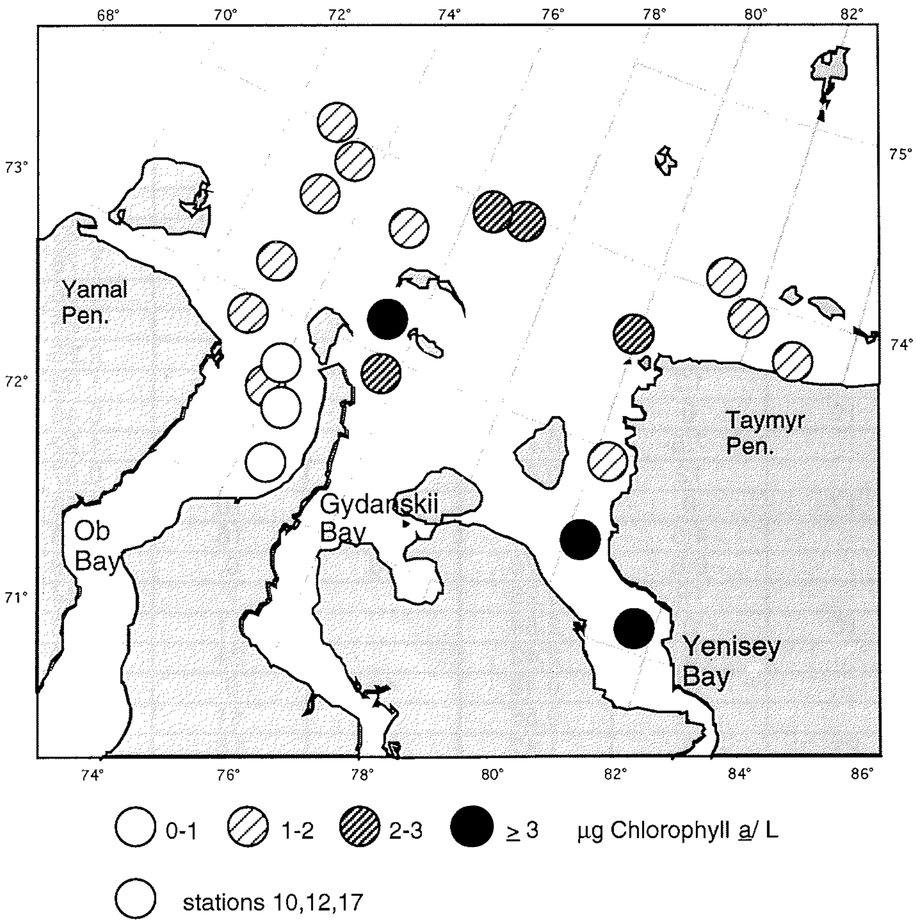

Fig. 3. Chlorophyll a concentrations (µg/L) in the surface waters during the expedition with RV "Akademik Boris Petrov" in 1997.

Chlorophyll a concentrations ranged from 0.21 to 3.13 µg/l (Table 2) with maximum values in the surface layers; higher phytoplankton biomass (surface and integrated values; Figs. 3, 4) was found in the eastern part of the investigation area. Similar results had been obtained by Vedernikov et al. (1995). Like Vedernikov et al. (1995) we found, except for some stations (again 10, 12, 17), an inverse relationship of surface chlorophyll a concentrations with surface salinity. For nitrate and other nutrients this relationship was not so pronounced leading to the conclusion that mixing of different water masses may have occurred in the investigation area. Indication for this might be the salinity values ranging around 10 and higher at most of the stations except the ones in the rivers (see also Churun and Ivanov, 1998). Another explanation could be that samples for nutrients and chlorophyll were taken from water bottles, salinity data came from the CTD which were run before. The analyses of phytoplankton species composition may give more information of the origin of water masses.

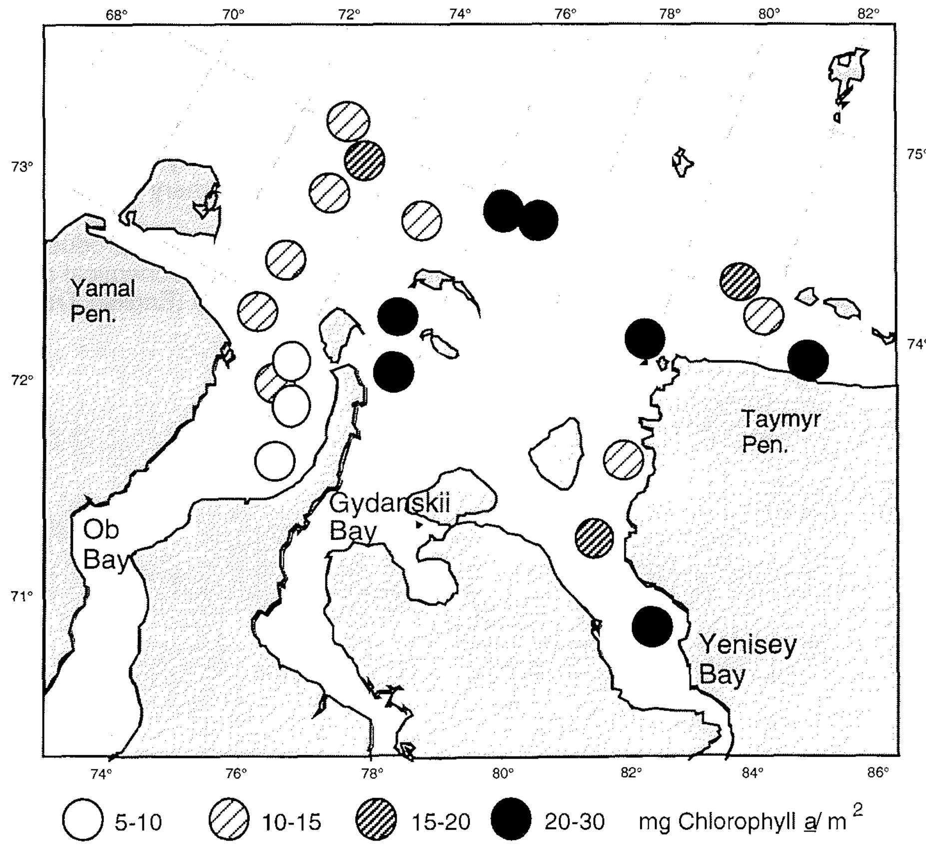

Fig. 4. Chlorophyll a concentrations (mg m^{-2}) integrated over the whole water column during the expedition with RV "Akademik Boris Petrov" in 1997.

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THE ROLE OF MESOZOOPLANKTON FOR THE TRANSFORMATION OF ORGANIC MATTER

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The aim of the zooplankton investigations was to describe the distribution of mesozooplankton species and the composition of communities along the salinity gradient caused by the strong freshwater input from the Siberian rivers Ob and Yenisei. Especially the determination of consumption rates using living animals in the laboratory will help to assess the importance of biological processes in the particle flux and transformation within the Kara Sea ecosystem.

Of special interest was the role of these zooplankters for the transformation of organic matter, brought into the Kara Sea by the rivers mostly as detritus. With the help of laboratory experiments with freshly captured animals some aspects of the feeding and life strategies were investigated. First, the *in situ* faecal pellet production which gives information about the current feeding situation. Preserved material can be analysed later for gut contents, faecal pellet composition, energy exploitation and transformation processes during digestion. The second topic was the study of in-situ egg production which mirrors at the same time the efficiency of feeding and the current reproductive state of the females. Fixed material can serve for analysis of gonad development.

A third aspect was the salinity tolerance of oceanic species towards low salinities. The freshwater signal of the estuaries extends many hundred miles northwards and influences the vertical and horizontal zooplankton distribution. The question in how far oceanic species are able to persist low salinities in order to feed on detritus in the oligohaline, detritus-rich surface layers was elucidated.

Material and Methods

Sampling
At 20 stations zooplankton samples were taken with a Nansen closing net of 150 µm mesh size, which was towed vertically with less than 0.5 ms^{-1} (Fig. 1). According to salinity 4 nets were deployed at each station: One net haul from below and above the pycnocline, respectively, were preserved in 4% buffered formaline. From the other two net hauls from the deep layers living animals were sorted out for experiments.

Experiments

I. In-situ faecal pellet production
48 *Calanus* CV (if available) and as many females as possible were kept individually in cell wells filled with filtered seawater, which was sampled in a large volume bathomat and filtered with cellulose-nitrate filters (0.45 µm). After 24 h

incubation in a refrigerator at about 20°C pellet production was controlled and pellets were fixed in formaline for each stage (CV, females) separately.

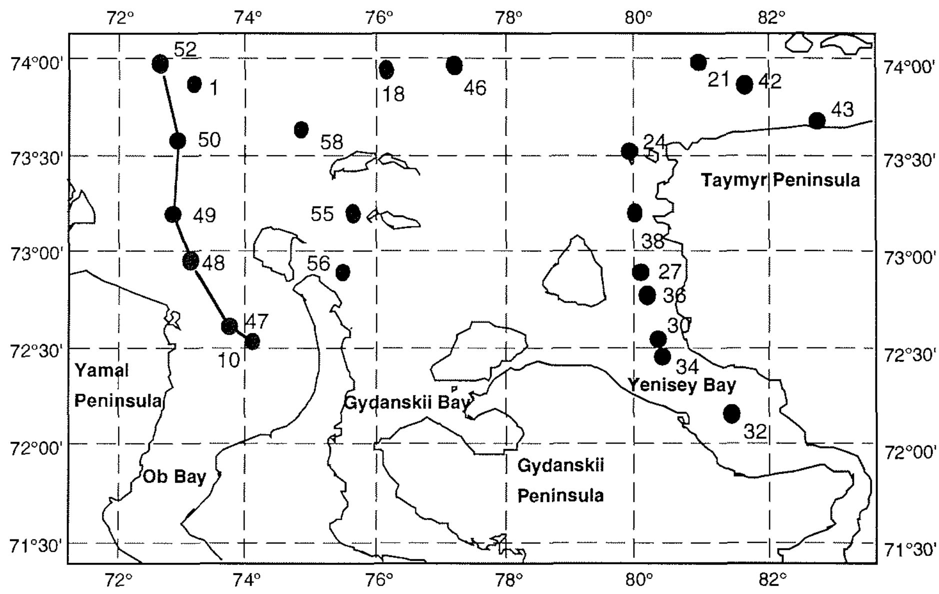

Fig. 1. Zooplankton stations in the Ob and Yenisei estuaries during the expedition with RV "Akademik Boris Petrov" in 1997. The line marks the Ob-Transect shown below.

II. In-situ egg production
For egg production experiments, individual females were incubated in cell wells for at least 24 hours at ambient temperatures. The wells were checked every half day for eggs.

III. Feeding experiments
At four stations (18, 27, 42, 50) all animals from the experiment I were fed several times a day with detritus-rich surface waters which was salted up to about 30psu with marine salt (except st. 18: 1psu). After 36-48 h incubation faecal pellet production was controlled.

IV. Salinity tolerance of Calanus glacialis
At stations 50 and 52, 30 CV and 20 females captured at 30 psu were incubated in 2 l beakers with artificially salted water and exposed to a dilution series from 22.5 psu down to 8 psu. Every 24 h dead animals were removed and salinity was lowered at 2.5 psu intervals by dilution with freshwater. At the end of the experiment all remaining animals were fixed in formaline for further species determination.

Table 1: Abundance and relative composition of zooplankton species in the Kara Sea during the expedition with RV "Akademik Boris Petrov" in 1997.

Taxa	Abundance/m2	% abundance	% taxa
Calanoidea			
Acartia longiremis	11	0.026	
Calanus glacialis	715	1.798	
Calanus finmarchicus	40	0.101	
Calanus hyperboreus	8	0.021	
Centropages hamatus	3	0.007	
Drepanopus bungei	23084	58.038	
Eurytemora sp.	1	0.003	
Jaschnovia brevis ?	103	0.258	
Jaschnovia tolli	184	0.462	
Limnocalanus macrurus	172	0.431	
Metridia longa	69	0.173	
Microcalanus pygmaeus	558	1.402	
Pareuchaeta glacialis	1	0.002	
Pseudocalanus spp.	1770	4.449	
Pseudocalanus acuspes	1968	4.948	
Pseudocalanus major	2333	5.865	
Temora longicornis	1	0.003	
Nauplii Copepoda	4116	10.349	88.337
Cyclopoida and Harpacticoida	0		
Harpacticoida spp.	1	0.002	
Cyclopina littoralis	550	1.383	
Microsetella norvegica	3	0.007	
Oithona similis	2856	7.180	
Oncaea borealis	148	0.371	
Oncaea cop.+ males	103	0.258	8.942
Euphausiacea			
Nauplii	1	0.003	
Amphipoda	0		
Hyperia galba	2	0.004	
Gammarida gen. sp.	0	0.001	0.005
Ostracoda	7	0.018	0.018
Mysidaceae	0		
Mysis oculata	4	0.010	0.010
Hydromedusae	0		
Aeginopsis laurentii	2	0.005	
Aeginopsis larvae	1	0.002	
Eumedusa birulai	1	0.002	
Euphysa flammea	2	0.005	
Halitholus yoldia-arcticae	2	0.005	
Obelia spp.	1	0.002	0.020
Ctenophora	3	0.008	0.008
Polychaeta			
Polychaeta juv.	15	0.037	
Polychaeta larvae	187	0.471	0.508
Pteropoda			
Limacina spp.	35	0.088	
Clione limacina	96	0.242	0.330
Bivalvia larvae	34	0.084	0.084
Gastropoda larvae	1	0.002	0.002

Table 1cont'd.

Taxa	Abundance/m2	% abundance	% taxa
Chaetognata			
Sagitta elegans	82	0.205	
Eukrohnia hamata	1	0.002	0.207
Appendicularia			
Fritillaria borealis	58	0.146	
Oikopleura vanhoeffeni	38	0.097	0.242
Echinodermata			
Plutei	103	0.259	
juv. Asteroida/Ophiuroida	308	0.774	1.033
Protozoa			
Synchaeta sp.	1	0.002	0.002

Results

General species distribution

A total of 17 taxa with 30 species was determined (Table 1), in copepods most copepodite stages were identified. Calanoida dominated the mesozooplankton with 88.3% of all specimens collected, followed by Cyclopoida and Harpacticoida (8.9%). *Drepanopus bungei* was the most abundant species (58%), followed by *Oithona similis* (7.2%), *Pseudocalanus major* (5.9%) and *Pseudocalanus acuspes* (5%). Meroplanktic larvae of Echinodermata, Polychaeta and Mollusca were also frequent.

Ob transect

The number of taxonomic groups was lowest at St. 10 (16). It increased dramatically within a few kilometers to 25 (St. 47) and remained constant at 26 from St. 48 on northward. Limnic species were restricted mostly to St. 10 (*Jaschnovia brevis*, *Pseudodiaptomus* spec., *Cyclopina litoralis*) or to stations 10 and 47 (*Jaschnovia tolli*, *Limnocalanus macrurus*) (Fig. 2a). Marine copepod species had a minimum at St. 10, but a maximum close by at St. 47. The most frequent copepod, the brackish water species *Drepanopus bungei*, had its maximum at stations 10, 47 and 48.

Along the whole Ob transect the majority off the zooplankton lived below the halocline (Fig. 2b). *Pseudodiaptomus* was the only species which preferred the upper layer, all other species were numerous below the halocline. A significant exception was St. 47, where *Calanus glacialis* and *Limnocalanus macrurus* were also more abundant in the surface layer.

In situ faecal pellet production of Calanus species

At all stations only CV produced faecel pellets and only very few pellets were produced per animal in 24 h. Maximum individual production rate was 8 pellets per day by a CV from St. 49. It was quite obvious that more faecal pellets were produced in the open sea than in the river estuaries, where sometimes none of the specimens produced any pellets.

In-situ egg production

At all stations none of the collected females produced any eggs.

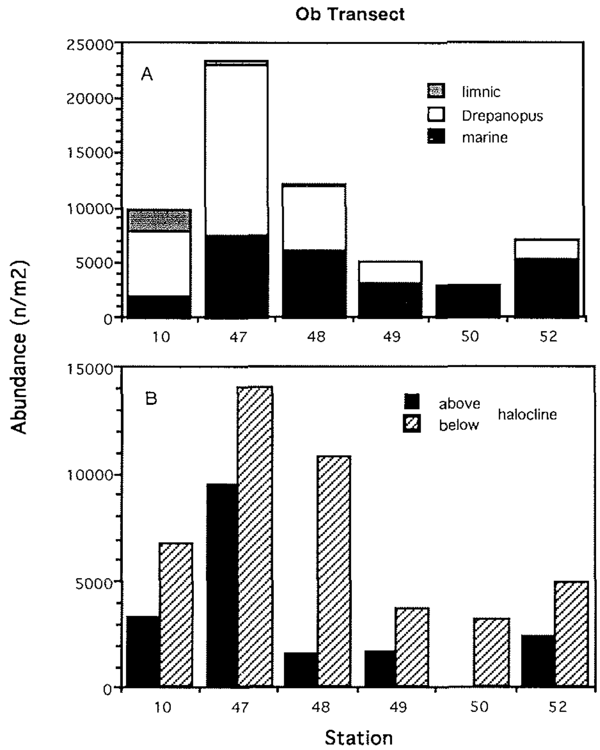

Fig. 2. Zooplankton composition along the Ob transect. Contribution of limnic and marine copepods together with *Drepanopus bungi* (A); vertical distribution of copepods in relation to the halocline (B).

Feeding experiments with Calanus species
In neither of the feeding experiments with surface waters faecel pellets were produced, neither by CV nor by females.

Salinity tolerance of Calanus glacialis
CV as well as female *Calanus glacialis* showed a rather high tolerance towards low salinities. From CV some specimens died first at 12 psu, three more at 10 psu and all others at 7.9 psu. The first female died at 17.4 psu, four more at 15 psu and another two at 12.4 psu. At 10 psu only three were still alive at the end of the experiments but nearly inactive.

Discussion

The zooplankton abundance was characterized by a relatively large number of taxa and species with an overwhelming dominance of copepods (96%). In the southernmost stations in the river Ob remains of a limnic copepod fauna were met, while further to the north a rich marine fauna was present, although in low numbers. There was a strong boundary between stations 10 and 47 in the Ob, which is not clearly reflected in the hydrographic data. Zooplankton species seem to be good indicators especially for water mass history.

The presence of oceanic species in the river mouths is striking. Further studies on their distribution in other parts of the Kara shelf, their salinity tolerance and feeding are necessary to decide, whether these forms are trapped and bound to die, or whether they exploit the rich food resources of the estuaries.

The brackish waters were dominated by the copepod *Drepanopus bungei.* This species is a typical brackish water form in Arctic marginal seas (Brodskii, 1967; Vinogradov et al., 1995a, b; Kosobokova et al., 1998), but its biology is little known.

A surprising observation is the preference of almost all species, both limnic and marine, for the water layer below the halocline although feeding conditions expressed in chlorophyll a were better in the surface layers (Nöthig and Kattner, this volume). In the future vertical migration and feeding habits have to be investigated in detail.

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BENTHOS COMMUNITIES: COMPOSITION, DIVERSITY PATTERNS AND BIOMASS DISTRIBUTION AS FIRST INDICATORS FOR UTILIZATION AND TRANSFORMATION PROCESSES OF ORGANIC MATTER

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The aim of the present study was to analyse the structure, species composition, abundance and biomass of benthic macrofauna (> 0.5 cm) communities along biotic and abiotic gradients in the estuaries of Ob and Yenisei. Although the benthic macrofauna was studied at species level by Russian scientists during former expeditions, neither the ecology nor the importance of these communities in the decomposition and transformation of organic and inorganic matter in the estuaries of large Siberian rivers has been studied at all.

Material and Methods

During the 1997 expedition of RV 'Akademik Boris Petrov' into the Ob and Yenisei estuaries (Kara Sea) macrobenthic organisms were sampled along different transects from north to south. The transect sampling was performed to study the influence of increasing river water on the distribution and composition of benthic communities.

At 26 stations a total of 52 quantitative macrobenthos samples at water depths between 10 and 40 m were taken. The sampling was performed by an OKEAN grab, covering an area of 0.25 m^2. Additional material for species diversity analyses was sampled by a small dredge (frame opening 100 x 30 cm, mesh size 0.5 cm) at 20 stations. All grab samples were washed in a sediment-washing-machine and passed through a 500 µm mesh size sieve, the dredge material was sieved with a 1000 µm screen. After sieving, the grab and dredge samples were bottled and preserved with buffered ($Na_2B_4O_7$) formaldehyde (7%). To avoid a decay of calcareous structures, all samples were transferred into 70% ethanol immediately after weighing.

The grab material was sorted and the wet weight (g ww) of the major taxa determined. For statistical analyses, the wet weight was recalculated to an area of one square metre. To avoid an overestimation of the bivalve biomass (shell weight), the weight of these animals was recalculated by a conversion factor (8.1 % of total ww equals soft tissue ww; Rumohr et al., 1987).

To determine the influence of abiotic factors, all biomass data were correlated with water depth, temperature, salinity, oxygen concentration and sediment characteristics available.

The biomass distribution along the transects was tested for significant differences by SANOVA and subsequent Post Hoc test of different means (a = 0.05).

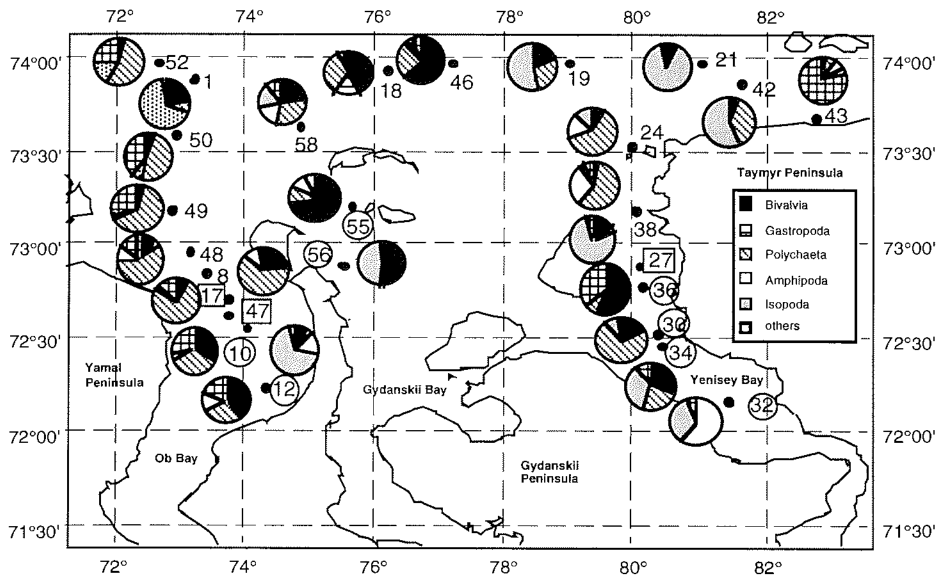

Fig. 1. Benthos stations sampled in the Ob and Yenisei estuaries during the expedition with RV "Akademik Boris Petrov" in 1997. The pie charts show the biomass relation between the most important major taxa. O - stations with salinities < 25 PSU and temperatures > 0°C; O + ® - stations with water depths < 20 m.

In further laboratory investigations all animals will be counted and determined to species level. Additional studies on aspects of the autecology of selected abundant species (e.g. population dynamics, feeding ecology, reproduction biology) will help to understand the role of key species in the transformation of organic matter in the estuaries of Ob and Yenisei.

Results

Figure 1 shows the location of the sampling stations and the biomass relation of the dominant major taxa. In 52 grab samples a total of 17 major taxa could be identified (Table 1, Fig. 2). Bivalves, polychaetes, cumaceans, amphipods and isopods showed the highest frequency of occurence and were present in more than 80 % of the grab samples. All other taxa were found in less than 45 % of the samples.

The total biomass per sample showed values between 0.24 and 149.6 g ww m^{-2} with a mean of 37.1 ± 32.6 g ww m^{-2}. Bivalves, polychaetes and isopods represented the dominant major taxa (Fig. 3) with maximum biomasses of 85.1, 52.2 and 79.6 g ww m^{-2}, respectively. Excluding amphipods and gastropods, all other major taxa were of minor importance in terms of biomass. First results of the species determination within the bivalves, isopods, amphipods and cumaceans indicate that *Portlandia aestuariorum*, *Mesidothea entomon*, *Pontoporeia affinis* and *Diastylis* sp. are the dominant species.

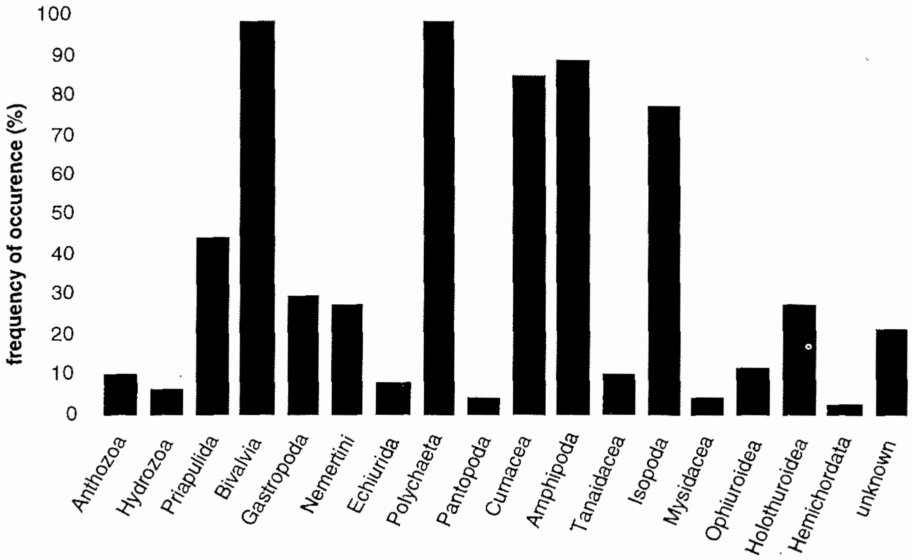

Fig. 2. Frequency of occurence of the major taxa in the grab samples (n=52) of the Ob and Yenisei estuaries in 1997.

Along the transect from north to south significant differences (a = 0.05) in the total biomass distribution as well as in the biomass distribution of gastropods and polychaetes were observed. At stations with reduced salinities (< 25 psu), bottom temperatures higher than 0 °C and water depths less than 20 m (Fig. 1) the biomass of these groups was significantly lower. Within the three main investigation areas the isopod biomass of the Yenisei Bay was significantly lower than in the Ob and Gydanskii Bay areas. However the total biomass as well as the biomass of bivalves, gastropods, polychaetes and amphipods showed no significant differences. The total biomass and the biomass of the major taxa was not correlated with local oxygen concentrations and sediment characteristics.

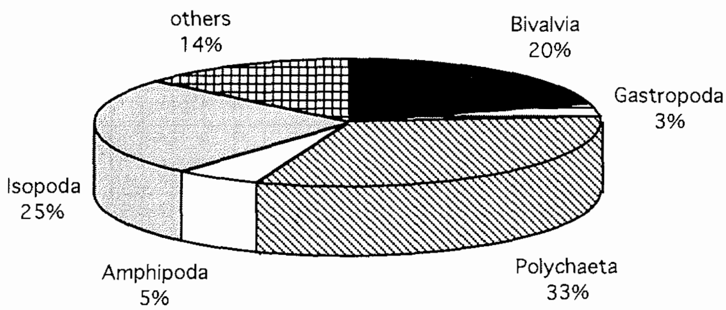

Fig. 3. Biomass relation between the most important major taxa.

Tab. 1: Biomass data (g wet weight) of the OKEAN-grab samples (area = 0.25 m2) from the Ob and Yenisei estuaries in 1997.

taxon/stat.	**1 (1)**	**1 (2)**	**8 (1)**	**8 (2)**	**10(1)**	**10(2)**	**12(1)**	**12(2)**	**17(1)**	**17(2)**	**18(1)**	**18(2)**	**19(1)**	**19(2)**	**21(1)**	**21(2)**	**24(1)**
Anthozoa											0.297	0.139					
Hydrozoa										0.004							
Priapulida	0.415		0.324	0.030			0.081	0.291		0.217							0.015
Bivalvia	49.085	56.355	3.016	7.208	0.396	0.700	7.271	3.497	21.292	12.047	262.617	86.103	9.243	22.433	0.530	6.343	4.780
Gastropoda				0.069						0.214	0.845	11.985	0.236				0.183
Nemertini						0.046			0.007		0.053	0.296					
Echiurida											0.591	0.152					
Polychaeta	1.331	2.043	1.567	6.524	0.028	0.037	0.152	0.440	3.193	4.680	13.046	9.937	1.366	2.697	0.982	0.114	1.812
Pantopoda											0.017						
Cumacea	0.004		0.124	0.082			0.011	0.037	0.017	0.025	0.674	0.488	0.013	0.020	0.007	0.002	0.023
Amphipoda	0.108	0.004	0.057	0.238		0.189	0.176	0.113	1.107	0.505	0.559	1.012	0.007	0.006	0.010	0.016	0.720
Tanaidacea				0.002						0.002		<0,001					
Isopoda	16.252	9.458	0.015			0.763			0.103	0.051	0.006	<0,001	7.307		0.509	19.889	1.319
Mysidacea																	
Ophiuroidea			0.751	0.051							0.041	0.099					
Holothuroidea												0.080			0.451	0.271	
Hemichordata																	
unknown				0.008								0.025					
total	67.195	67.860	5.854	14.212	0.424	1.735	7.691	4.378	25.719	17.745	278.746	110.316	18.172	25.156	2.489	26.635	8.852

note that biomass values for bivalves are not recalculated by conversion factor of 0.081

Tab. 1 (cont.): Biomass data (g wet weight) of the OKEAN-grab samples (area = 0.25 m2) from the Ob and Yenisei estuaries in 1997.

taxon/stat.	24(2)	27(1)	27(2)	30(1)	30(2)	32(1)	32(2)	34(1)	34(2)	36(1)	36(2)	38(1)	38(2)	42(1)	42(2)	43(1)	43(2)
Anthozoa																	
Hydrozoa																	
Priapulida				0.185	0.029	0.862	0.009	0.811	0.795	0.021	0.425		0.097	0.012		19.847	
Bivalvia	4.705	6.936	5.401	14.778	12.356	0.381		27.407	32.801	11.259	21.852	2.021	1.708	4.091	14.135	1.985	0.182
Gastropoda											0.059			0.481	0.132		
Nemertini		0.017	0.042							1.308							
Echiurida																	
Polychaeta	5.090	0.231	0.110	4.016	3.969	0.049	0.035	2.065	1.785	0.131	0.189	2.359	1.807	4.440	7.644	1.703	0.305
Pantopoda																	
Cumacea	0.041			0.034	0.035		0.002	0.192	0.156		0.006	0.001	<0,001	0.085	0.109	0.001	0.001
Amphipoda	1.012			0.022		3.884	4.801	0.040	0.033			0.947	1.143	0.163	0.144	0.030	1.981
Tanaidacea																	
Isopoda	0.032	4.223	0.927		1.158		5.393	4.931	0.525			0.270	0.027	17.808	1.179	0.005	0.695
Mysidacea									0.013		0.010						
Ophiuroidea																	
Holothuroidea	0.017											0.166	0.232	0.003	0.093		
Hemichordata			0.226														
unknown	0.003	0.013	0.036									<0,001	<0,001				
total	10.900	11.420	6.742	19.035	17.547	5.176	10.240	35.446	36.108	12.719	22.541	5.764	5.014	27.083	23.436	23.571	3.164

Tab. 1 (cont.): Biomass data (g wet weight) of the OKEAN-grab samples (area = 0.25 m2) from the Ob and Yenisei estuaries in 1997.

taxon/stat.	46(1)	46(2)	47(1)	47(2)	48(1)	48(2)	49(1)	49(2)	50(1)	50(2)	52(1)	52(2)	55(1)	55(2)	56(1)	56(2)	58(1)	58(2)	total
Anthozoa						0.019			12.554		7.372							0.111	20.492
Hydrozoa			0.004	0.002															0.010
Priapulida				1.218	0.225										0.187	0.235	1.088		27.419
Bivalvia	61.456	40.072	6.231	13.033	4.750	16.040	10.465	5.001	6.567	16.344	0.901	7.881	47.883	26.281	89.395	72.278	34.239	34.573	1208.304
Gastropoda	0.072					0.615		0.103	0.126								0.077	0.365	15.562
Nemertini	0.005			0.004	0.003	0.019									0.022		0.010	0.016	1.848
Echiurida								5.936									1.088		7.767
Polychaeta	1.998	1.140	0.339	1.292	3.921	4.991	6.365	9.053	5.377	9.818	8.647	7.594	0.736	0.201	0.670	0.169	7.828		156.016
Pantopoda											<0,001								0.017
Cumacea	0.151	0.005	0.009	0.026	0.304	0.238	0.091	0.041	0.014	0.016		0.005	0.021	0.016	<0,001	0.010	0.065	0.161	3.363
Amphipoda	0.028	0.239	<0,001	0.001	1.165	0.205	0.076	0.163	0.032	0.092	0.067	0.116	0.432	0.301	<0,001	<0,001	1.807	2.463	26.214
Tanaidacea					<0,001	0.002													0.006
Isopoda	0.535			0.226	0.057	0.002	0.224	1.333	1.403	0.489	5.389	0.032	0.593	0.016	0.141	12.457		4.593	120.335
Mysidacea																			0.023
Ophiuroidea					0.646	0.893													2.481
Holothuroidea	0.007	0.585			0.006	0.005											0.276	0.046	2.238
Hemichordata																			0.226
unknown						0.020									0.016		0.020	0.022	0.033
total	64.252	42.041	6.583	15.802	11.077	23.049	17.221	21.630	26.073	26.759	22.376	15.628	49.665	26.815	90.431	85.149	46.498	42.350	1592.354

Discussion

Zenkevitch (1963) reported benthic biomasses in the shallows of the Yamal Peninsula of about 100-200 g ww m^{-2}, close to the results of the present study (ca. 150 g ww m^{-2}). However the central part of the Kara Sea shows only biomass values of ca. 5 g ww m^{-2} (Zenkevitch, 1963) and is therefore less productive as the estuaries of Ob and Yenisei. Hence the estuaries of these two large Siberian rivers represent high productive areas which underlines that they play an important role in the transformation of organic matter within the Kara Sea ecosystem.

Similar to Cochrane et al. (1997) the results of our study indicate that mainly three major taxonomic groups - molluscs, annelids and crustaceans - are dominant in the estuaries of the Siberian rivers Ob and Yenisei. Beside bivalves, polychaetes and isopods the amphipods and cumaceans were also frequently found in the grab samples. Because of the small body size of the most abundant species in the last two groups, their portion of the total biomass is, however, only small. Bivalves, polychaetes and isopods together contribute about 80 % of the total biomass and therefore play an important role within the estuarian biocoenoses of the investigated rivers.

Differences along the north-south transects confirm the existence of gradients in the biomass distribution with decreasing water depth, increasing temperature and fresh water influence. The total biomass was mainly influenced by salinity, temperature and water depth. At increasing salinity and water depth together with lower temperatures at the sea floor the total biomass increased. Gastropods and polychaetes followed this general trend, whereas the biomass of the other major taxa might be influenced by other parameters, such as food supply, seasonal variation, bottom structure, etc.. The sediment characteristics, usually a major factor governing composition and distribution of benthic communities, can be probably neglected because of its uniformity in the Ob and Yenisei estuaries.

Echinoderms, usually the dominant benthic taxon in higher latitudes (Piepenburg, 1989; Piepenburg and Juterzenka, 1994), were only rarely found in our samples and only at deeper stations (> 20 m) with at least 30 psu salinity and bottom temperatures below 0 °C. These findings stand somehow in contradiction to results previously published by others that brittle stars dominate epibenthic communities on Arctic shelves (see Piepenburg and Schmid, 1996). Although meroplanktic larvae of echinoderms were identified in the zooplankton samples (see Halsband and Hirche, this volume) the very low number of ophiurids and holothurians at the bottom indicate the influence of brackish water as the most probable limiting factor for these animals (Cochrane et al., 1997). This raises the question which species fill up the gap in carbon utili-zation, at least seasonally, if one of the major megafauna elements is missing in the benthic energy flow?

Portlandia estuariorum, *Mesidothea entomon*, *Pontoporeia affinis* and *Diastylis* sp. represent, together with unidentified polychaetes, the dominant species in the investigated area. Apart from *M. entomon*, which preys as a top predator mainly on polychaetes and crustaceans (Gruner et al., 1993), all other species and most of the polychaetes are known as deposit feeders (Hartmann-Schröder, 1996). Thus, these species seem to keep a key position in the estuarine food web of Ob and Yenisei (Khlebovich and Komendantov, 1997) and have to be studied in detail concerning their role in the transformation of the outcoming fluvial organic matter.

In conclusion, the benthic biomass of the Ob and Yenisei estuaries are very high in comparison to the deeper part of the Kara Sea and dominated by only few major taxa. Several species of polychaetes and especially the bivalve *Portlandia aestuariorum* as deposit feeders represent, beside planktonic organisms and bacteria, the most important biological components in utilization and transformation of fluvial organic matter. Further identification of key species, investigations of their population dynamics, reproduction biology and feeding ecology and especially the determination of consumption rates on living animals in the laboratory will help to assess the importance of biological processes in the particle flux and transformation within the Kara Sea ecosystem.

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BENTHIC FORAMINIFERA IN THE OB ESTUARY, WEST SIBERIA

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Abstract

Freshwater discharge of River Ob forms a salinity-gradient zone, which extends over hundreds of kilometers in the southern Kara Sea. The study was aimed to analyse the shifts in benthic foraminiferal fauna through the salinity gradient. A transect of nine stations, sampled in September 1997 during the RV 'Akademik Boris Petrov' cruise, extended from the inner Kara Sea to the Ob estuary. The principal faunal boundary occurred at the depth break 15 to 30 m. In the shallower inner area, the near-bottom salinity was 20 to 25‰ being subject to seasonal and synoptical variation. A low-diverse foraminiferal assemblage was dominated by Allogromiina followed by *Elphidium excavatum* f. *clavata* and *Protelphidium orbiculare*. In the deeper outer area with slightly reduced near-bottom salinities (32‰), there were four dominant populations (*Reophax curtus, Ammotium cassis, Elphidium excavatum* f. *clavata* and *Eggerella advena*) replacing one another in the offshore direction. The available environmental data are insufficient to explain the succession. *Elphidiella tumida*, *Elphidium asklundi/incertum, Buccella frigida* and *Cassidulina reniforme* declined within a steep salinity gradient from 30 to 25‰ whereas *E.e. clavata* and *P. orbiculare* tolerated 20‰ and perhaps lower. A comparison with earlier foraminiferal studies indicates that the distribution of the dominant taxa is persistent on a year-to-year scale.

Introduction

Two large Siberian rivers, Ob and Yenisei, discharge into the Kara Sea delivering yearly 1160 km^3 of fresh water which accounts for 30% of the annual fresh-water influx to the Arctic Ocean (Aagard and Carmack, 1989). This tremendous runoff, mixing with seawater, forms a vast salinity-gradient zone, which occupies the outer Ob and Yenisei estuaries and the adjacent Kara Sea (Burenkov and Vasilkov, 1994). In this study I analyze the distribution of modern foraminifera along a transect of nine stations from the outer Ob estuary to the inner Kara Sea. The goal of the research was to study the changes in the foraminiferal fauna along the salinity gradient. The results will eventually improve our understanding of Arctic foraminiferal ecology.

Material and methods

Nine north-south aligned stations compose a transect from the outer Ob estuary to the inner Kara Sea (Fig. 1). The samples were collected 13-24 September 1997 during the Russian-German expedition by RV "Akademik Boris Petrov" to the southern Kara Sea (Table 1). The sediment was retrieved with a multi corer (the standard 12-tubes version, 6-cm inner tube diameter). The sediment surface was visually undisturbed in most cases. The topmost 1-cm layer from two cores was combined into a sample. Thus each sample represented 30+30=60 cm^2 surface area and ca. 60 cm^3 (measured) wet sediment volume. Two samples per station were taken with one of them being processed for this study. The sediment was preserved in five volumes of 96% methanol stained with Rose Bengal. Due to admixture of pore water, a final concentration of methanol in the preserved samples was ca. 75%. To keep intact the chitinous and fragile agglutinated tests the treatment employed no drying. Foraminifera from the size fraction >0.125 mm were examined in water under a dissecting microscope with transmitted and incident light. The counts of living (Rose Bengal stained) and dead (unstained) specimens were normalized to 10 cm^3 (Murray, 1991).

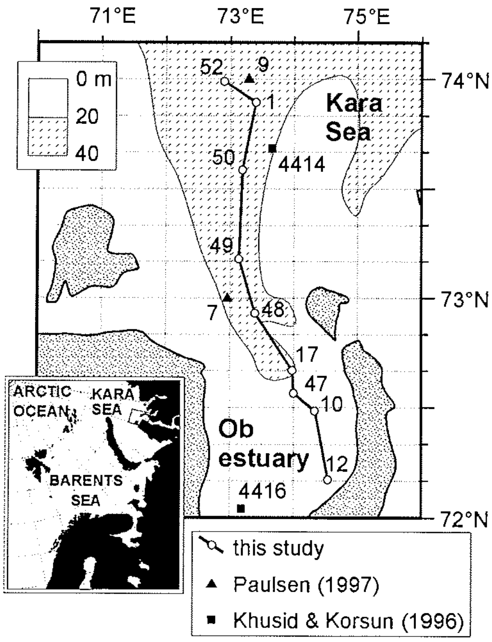

Fig. 1. Location of the sampling stations.

Study area

Water depth in the outer part of the transect is ca. 30 m whereas the inner section is shallower with depths of 15 m (Fig. 2A). At the time of sampling the seasonal pycnocline was at a water depth of ca. 10 m (Churun and Ivanov, 1998). In the deeper northern part of the transect, near-bottom salinity was ca. 32‰ and decreased down to 20‰ on the shallow. Near-bottom temperature in the same direction increased from -1.4 to 2°C (Fig. 2B). A high-gradient frontal zone occurred at the depth break on September 13 through 15. A week later, however, the frontal zone was not observed (Churun and Ivanov, 1998).

Table 1. Station list.

St.	N		E		depth (m)	date & time	
52	74°	00.02'	72°	39.72'	30.6	24.09.1997	1:55
1	73°	54.64'	73°	10.93'	28.5	13.09.1997	19:30
50	73°	36.66'	72°	57.08'	28.0	23.09.1997	8:50
49	73°	12.57'	72°	53.68'	29.6	23.09.1997	2:20
48	72°	57.68'	73°	08.86'	29.3	22.09.1997	12:45
17	72°	41.32'	73°	43.84'	20.7	15.09.1997	18:00
47	72°	35.01'	73°	44.91'	18.0	22.09.1997	7:50
10	72°	30.02'	74°	04.86'	15.0	14.09.1997	18:00
12	72°	10.52'	74°	17.63'	13.4	15.09.1997	9:00

Fine-grained sediments dominate the study area. An upper oxidized layer 2 to 6 cm thick is of a brown color (Matthiessen et al., 1998). Sedimentological characteristics change abruptly between stations 47 and 10. At this boundary the sediment becomes much finer (Fig. 2C), there is a distinct increase in total organic carbon content (Fig. 2D), while $CaCO_3$ concentration drops to an instrumental zero (Fig. 2E) (cf. Müller and Stein, this volume; Boucsein et al., this volume).

Results

Taxonomy

A total of 31 foraminiferal taxa were distinguished in the samples including 7 soft-shelled allogromiids, 11 arenaceous species and 13 calcareous (Table 2). No planktic foraminifera were recorded. Seven clearly distinct forms of soft-shelled foraminifera were present in the material. There are no regional data on the taxonomy of this group and I designated these forms as Allogromiina species 1 through 7 (Table 2). All the arenaceous and calcareous species are well known taxa described and illustrated in a number of monographs on Arctic and Subarctic foraminifera (Höglund, 1947; Loeblich and Tappan, 1953; Barker, 1960; Knudsen, 1971; among others). However, two forms, *Reophax curtus* and *Elphidium asklundi/incertum*, need some comments.

Apart from typical specimens of *Reophax curtus* there were smaller unilocular and bilocular tests resembling *Reophax scorpiurus* and *Reophax atlantica*. They have been counted as juvenile *Reophax curtus.*

Elphidium asklundi and *Elphidium incertum* are often difficult to separate owing to the absence of a morphological hiatus. Most of the specimens were typical *Elphidium asklundi* and a few tests were transitional to *Elphidium incertum.*

Foraminiferal distribution

The number of foraminifera decreased steadily inshore (Fig. 2F). In the same direction three dominant arenaceous species subsequently replaced each other, *Eggerella advena* (northernmost), *Ammotium cassis* and *Reophax curtus* (Fig. 2J,K,L). The arenaceous fauna entirely declined at 72°35'N latitude. Several calcareous taxa also disappeared close to the same boundary –

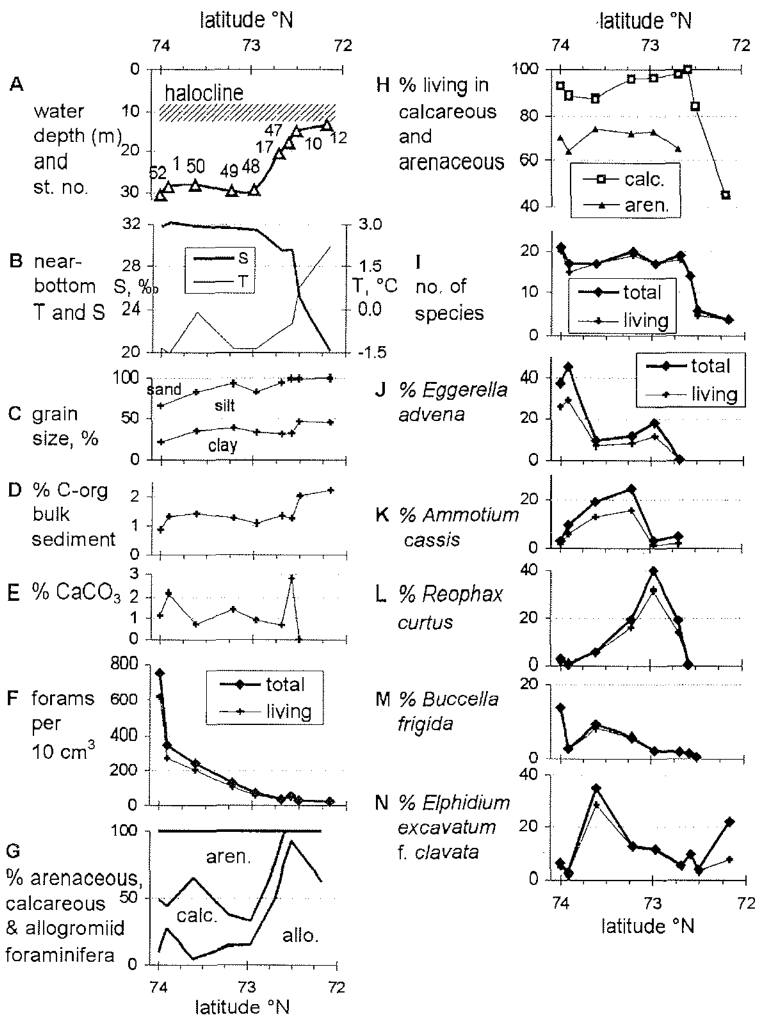

Fig. 2. Distribution of selected foraminiferal taxa, faunal characteristics and environmental variables along the Ob transect. The area between the 'living' and 'total' curves represents the contribution of dead (unstained) foraminifera. The temperature and salinity data is from Churun and Ivanov (this volume), C_{org} and $CaCO_3$ from Boucsein et al. (this volume) and grain size from Müller and Stein (this volume).

Buccella frigida, Elphidiella tumida, Elphidium asklundi/incertum and *Cassidulina reniforme* (Table 2). Consequently, the faunal diversity dropped at the 72°35'N boundary (Fig. 2I). *Elphidium excavatum* f. *clavata* and *Protelphidium orbiculare* occurred along the whole transect (Table 2). The number of soft-shelled foraminifera showed no evident trend through the transect. Their frequency, however, reached up to 63-93% at the inner stations due to the decline in arenaceous and calcareous foraminifera (Fig. 2G).

Virtually all (99 to 100%) allogromiids were alive (stained). The percentage of living individuals in the arenaceous fauna was rather stable throughout the transect ranging from 64 to 74% with no obvious trend (Fig. 2H). This index in the calcareous foraminifera was high in the inner Kara Sea (>88%), still increasing southward up to 100% at st. 47, and then perceptibly decreasing further south (Fig. 2H).

Dissolution signs occurred in both living and dead calcareous specimens. The portion of partially dissolved tests differed remarkably between the species. All individuals of the miliolid foraminifera – *Pyrgo williamsoni* and *Quinqueloculina* sp. – were etched by dissolution. In contrast, none of *Buccella hannai arctica* and *Guttulina sp.* was dissolved (Fig. 3). The occurrence of partially dissolved specimens in the other calcareous taxa increased landward in the outer part of the transect and then decreased south of 72°35'N at the two innermost stations.

Discussion

Foraminiferal distribution

The analysed faunal characteristics outline a boundary at 72°35'N latitude. There is a three-fold decrease in the foraminiferal diversity accompanied by the complete disappearance of arenaceous taxa; the percentage of allogromiids increases dramatically (Fig. 2G). Thus this faunal change close to 72°35'N latitude marks a boundary between two foraminiferal faunas, inner and outer ones. Even though the transition is sharp, it remains continual extending over three closely located stations, 17, 47 and 10 (Fig. 4). This faunal boundary is associated with abrupt changes in the measured environmental variables, grain size, C_{org} content, $\%CaCO_3$ and oceanographic characteristics (Fig. 2B-E).

Salinity of near-bottom water is likely to be a principal environmental clue controlling the foraminiferal distribution in the estuary. The evident faunal boundary at 72°35'N coincides with the depth break. In the shallower inner zone (15-m deep), the halocline contacted the seafloor resulting in decreased near-bottom salinities of 20-25‰. The oceanographic boundaries in the estuary migrate vertically and horizontally on a synoptic time-scale (Churun and Ivanov, 1998). When the surface brackish layer eventually thickens some five meters more, it will rest on the seafloor. Only few opportunistic species can survive and thrive in such harsh environment. Therefore the abrupt decrease in foraminiferal diversity seems to be controlled by the halocline depth.

In the outer zone, arenaceous taxa dominate the foraminiferal fauna with the only exception of st. 50 dominated by a calcareous species, *Elphidium excavatum* f. *clavata*. The sequence of the dominant species in the outer zone does not seem to be associated with any tendencies in the recorded environmental variables including near-bottom salinity (Fig. 2). The sequence may rather reflect different trophic conditions owing to the different distance to the frontal zone where most of the organic carbon accumulates (Lisitsyn et al., 1995).

Table 2. Benthic foraminifera (Living+dead=total percentage) along the Ob transect.

	st. #	52	1	50	49	48	17	47	10	12
1	Allogromiina sp.1	8	27	5	3	11	38	73	90	63
2	Allogromiina sp.2	2						1	3	
3	Allogromiina sp.3				5	3	8	2		
4	Allogromiina sp.4						1			
5	Allogromiina sp.5						<1			
6	Allogromiina sp.6						<1	<1		
7	Allogromiina sp.7				7	<1	1			
8	*Hippocrepinella sp.*			1	<1			<1		
9	*Crithionina sp.*				3	5	<1			
10	*Reophax curtus*	2	<1	5	19	40	19	<1		
11	*Reophax scottii*	<1								
12	*Reophax dentaliniformis?*	1			1			<1		
13	*Cuneata arctica*	4	<1		1					
14	*Ammotium cassis*	3	10	19	25	3	5			
15	*Cribrostomoides jeffreysi?*	1	<1							
16	*Spiroplectammina biformis*	1	<1	<1	2	1	<1			
17	*Textularia torquata*	2		<1	1					
18	*Eggerella advena*	38	45	9	11	18	<1			
19	*Quinqueloculina sp.*	1	<1			<1	1	<1		
20	*Pyrgo williamsoni*				<1	<1				
21	*Glabratella wrightii*	<1								
23	*Buccella frigida*	14	3	9	6	2	2	1	1	
22	*Buccella hannai arctica*	5	5	5				3	1	
24	*Elphidiella tumida*		<1	1	<1	<1	<1	1		
25	*Protelphidium orbiculare*	3	1	4	1	1	9	5		15
26	*Elphidium asklundi/incertum*	3	4	3	1	<1	2			
27	*Elphidium bartletti*			<1						
28	*Elphidium excavatum f. clavata*	6	2	35	12	11	5	9	3	22
29	*Cassidulina reniforme*	6	<1	1	1	<1	1			
30	*Guttulina sp.*	1	1	1	<1	1	4	4	3	1
31	*Lagena gracillima*	<1	<1	<1						
	benthics/10cm3	755	349	243	131	72	34	56	30	21
	benthics counted	317	314	292	314	301	202	336	177	123
	no. of species	21	17	17	20	17	19	14	6	4
	% living	82	78	84	82	81	90	99	99	80
	% calcareous	39	17	61	23	18	25	23	7	37

The foraminiferal fauna of the outer zone lacks a number of taxa common of the open Kara Sea, such as *Portatrochammina bipolaris* Brönnimann & Whittaker (redescribed from *Trochammina nana* Brady), *Reophax pilulifer, Labrospira crassimargo, Cribrostomoides subglobosum, Recurvoides turbinatus* and *Elphidium subarcticum* (Hald and Steinsund, 1996; Khusid and Korsun, 1996; Paulsen, 1997). This lack of open-sea species can be considered indicative of decreased bottom salinities of ca. 32‰ observed in the northern part of the transect.

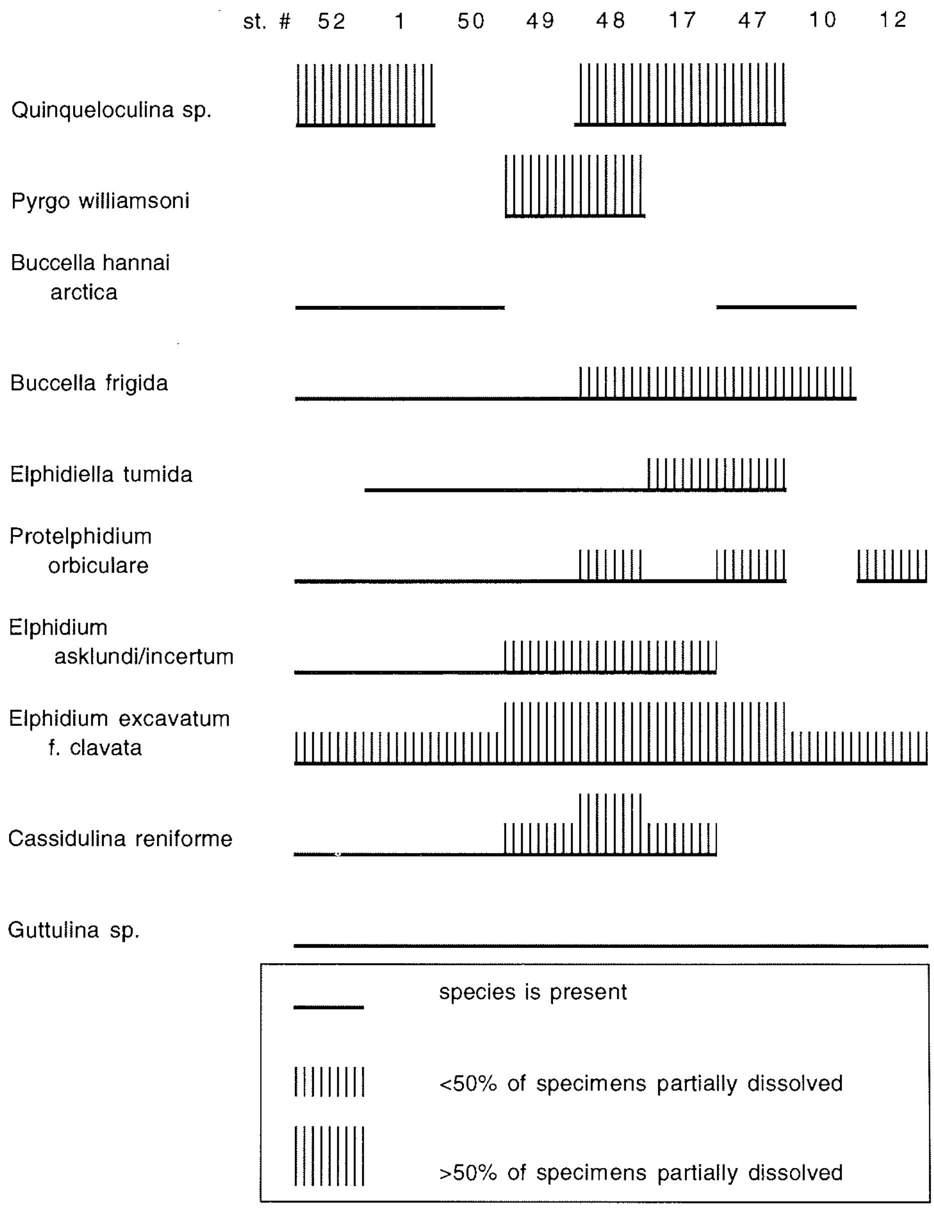

Fig. 3. Dissolution of calcareous foraminifera on the Ob transect. Both living and dead specimens are included.

Elphidium subarcticum and *Elphidium albiumbilicatum* (often combined under a single species name) commonly occur in subtidal hypohaline habitats of the Barents and Kara seas and thus have been thought typical of decreased salinities. The absence of these species in the study area suggests that there is another still unknown environmental factor that prevents these foraminifera from penetrating into the estuary.

Eggerella advena occurs in the Barents Sea only in shallow areas, mostly <100 m (Digas, 1970; Korsun et al., 1994). As these shallow areas are dominated by sandy sediments in the Barents Sea, the species has been considered characteristic of sands. The high occurrence of *Eggerella advena* in the mud of the Ob estuary suggests that water depth (indirectly, through a still unknown factor) rather that sediment type controls the vertical distribution of the species on the Barents-Kara shelf.

The predominance of allogromiids is characteristic of the inner zone. Most foraminiferal studies omit Allogromiina owing to their low fossilization potential, and the ecology of this group is poorly known. The allogromiid foraminifera are generally thought opportunistic but there is little evidence to support this understanding (e.g. Lambshead and Gooday, 1990). The assumption of the opportunistic nature of allogromiids would explain their dominance in the inner zone where the habitat is stressed by periodical freshening and less tolerant foraminifera are suppressed or eliminated.

Paleosalinity

Micropaleontological studies rely mainly on calcareous foraminifera as they have high fossilization potential. Fossilization of the inner foraminiferal fauna will result in an assemblage consisting of *Elphidium excavatum* f. *clavata* and *Protelphidium orbiculare* because allogromiid tests rapidly decay. Such an assemblage from Quaternary records would characterize reduced paleosalinities – till at least 20‰ and likely lower.

Two calcareous species typical of low-saline habitats, *Elphidiella tumida* and *Elphidium asklundi/incertum*, decline close to the 72°35'N boundary. *Buccella frigida* and *Cassidulina reniforme* demonstrate the same range (Table 2, Fig. 4). A fossil assemblage lacking the above taxa but including *Protelphidium orbiculare* would correspond to a salinity fall below 25-30‰.

The exact salinity ranges, which different foraminiferal species can tolerate, are impossible to establish because of two reasons. First, the survey was carried out in September whereas the lowest salinities of the flood (May-June) must be critical. Second, infaunal foraminifera can survive freshening events burrowing deeper into the sediment where the salinity of pore water is supposed to be higher.

Dissolution of calcareous foraminifera

A high percentage of living specimens in the studied calcareous fauna (mostly 85-100%, Fig. 2H) indicates that empty tests are rapidly removed from the sampled topmost 1 cm of sediment. This may result from three processes: winnowing, rapid sediment accumulation and $CaCO_3$ dissolution. Winnowing of empty tests due to turbulent transport is very unlikely in the study area because this mechanism is characteristic only of sandy bottoms (Murray, 1987). Rapidly accumulating sediment (centimeters per year) would bury dead (and hence immobile) tests thus enlarging the portion of living (mobile) specimens. Based on Pb-210 dating, J. Carroll (personal communication, 1998) reported 0.1 mm/yr for the upper 50 cm sediment layer at the Ob mouth. M. Levitan and L. Polyak (personal communication, 1998), based on AMS radiocarbon dating, estimated the Holocene sedimentation rate at st. 4414 (see Fig. 1 for location) as 0.4 mm/yr. In any case, both values are far too low to affect the living/dead ratio. Therefore, the dissolution of dead tests is the only factor able to cause the observed high percentage of living calcareous specimens (cf. Hald and Steinsund, 1992).

The percentage of living specimens in the calcareous fauna tended to increase toward the faunal boundary at 72°35'N (Fig. 2H). There was the same tendency in the occurrence of partially dissolved specimens (Fig. 3). Both indexes point that dissolution of calcareous foraminifera reaches maximum at stations 17 and 47. The foraminiferal dissolution signal, however, accords with neither the %$CaCO_3$ curve nor C_{org} (Fig. 2D,E).

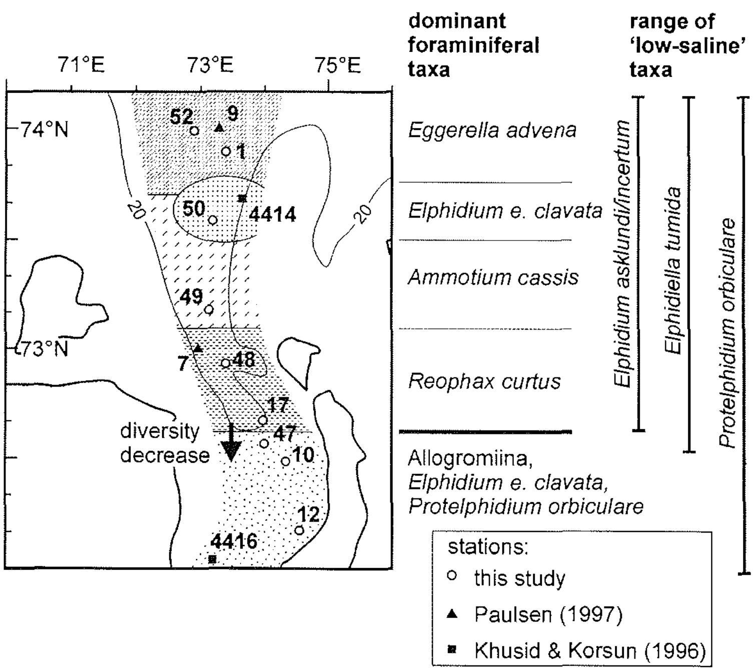

Fig. 4. Generalized distribution of benthic foraminifera along the Ob transect. The principal faunal change is associated with the depth break at latitude 72°35' N and extends over stations 17, 47 and 10.

A large number of living individuals bears dissolution signs. Many stained *Elphidium excavatum* f. *clavata* tests are largely devoid of calcite. Paulsen (1997) and Khusid and Korsun (1996) have made similar observations in the Ob and Yenisei estuaries. The loss of a part of the internal skeleton seems to be absolutely abnormal for living organisms and this arises a suspicion whether the partially dissolved specimens were actually alive at the time of sampling. Several authors have questioned the reliability of the Rose Bengal staining technique (see Jorissen et al., 1995 for review). In cold water, the remineralization of organic matter is slow and so dead foraminifera can remain stainable for months (Bernhard, 1988; Corliss and Emerson, 1990). It suggests that there could be an overestimation of the foraminiferal standing crop in this study.

Comparison with previous studies
Four stations of two recent foraminiferal studies (Khusid and Korsun, 1996; Paulsen, 1997) are located in the vicinity of the 1997 transect (Fig. 1). Both sampling programs had been completed precisely four years before, in September 1993. There is a good accordance between years 1993 and 1997 in the distribution of dominant taxa (Fig. 4); only the allogromiids cannot be compared as they have been omitted in the cited studies. Thus, there seem to be little year-to-year variation in the composition of dominant species.

Conclusions

The most evident discontinuity in the foraminiferal distribution along the transect occurs at 72°35'N where water depth decreases 30 to 15 m so that the halocline comes in contact with the seafloor. All arenaceous and some calcareous taxa decline at this boundary. South of the boundary a low-diverse foraminiferal assemblage is dominated by Allogromiina followed by *Elphidium excavatum* f. *clavata* and *Protelphidium orbiculare*. North of 72°35'N there is a sequence of four dominant population, *Reophax curtus, Ammotium cassis, Elphidium excavatum* f. *clavata* and *Eggerella advena*. The measured environmental variables are insufficient to explain the sequence.

The results on salinity tolerance are applicable in paleoenvironmental reconstructions. *Elphidiella tumida, Elphidium asklundi/incertum, Buccella frigida* and *Cassidulina reniforme* disappear at 25-30‰ whereas *Protelphidium orbiculare* and *Elphidium excavatum* f. *clavata* persist till 20‰.

Dissolution largely affects the calcareous fauna being most intense near the faunal boundary at 72°35'N. It is still unclear which factor causes the increase in dissolution rate of calcareous tests near the faunal boundary.

A comparison with earlier foraminiferal studies indicates that the distribution of dominant taxa in the estuary is persistent over time.

Acknowledgements

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PALYNOMORPHS IN SURFACE WATER OF THE OB AND YENISEI ESTUARIES: ORGANIC-WALLED TRACERS FOR RIVERINE WATER

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Introduction

Freshwater algae which contain organic compounds in their tests, cyst walls or coenobia have been frequently identified in late Quaternary sediments from high northern latitudes during routine palynological analyses (e.g. Hill et al., 1985; Mudie, 1985, 1992; Matthiessen, 1991,1995, this volume; Kunz-Pirrung, 1998, in press). In particular, the chlorococcalean algae *Pediastrum* and *Botryococcus* are abundant in shelf and deep-sea sediments of the Arctic Ocean (Hill et al., 1985; Mudie, 1985; 1992; Kunz-Pirrung, 1998, in press) suggesting that they might be useful tracers of freshwater discharge. Terrestrial palynomorphs such as pollen and phytoclasts often co-occur with these freshwater algae (Mudie, 1985; Kunz-Pirrung, 1998a,b; Naidina and Bauch, in press). These palynomorphs may be entrained into sea ice in the shallow coastal zones during freeze-up in autumn or may be discharged onto the landfast ice when the rivers break up in spring, being then transported into the central Arctic Ocean. Consequently, the occurrence of freshwater algae in deep-sea sediments of the Arctic Ocean and the Norwegian-Greenland Sea is attributed to the transport by sea ice and melt-out in spring (Mudie, 1992; Matthiessen, 1991,1995; Kunz-Pirrung, 1998, in press).

However, the occurrence of freshwater terrestrial palynomorphs in surface sediments can not unequivocally be related to riverine influx, because they may be reworked due to their good preservability from older deposits exposed along the coast line, at river beds or their banks. Unfortunately, the distribution of palynomorphs in surface waters in relation to freshwater discharge from the large Siberian rivers is little known. One of the few examples is the study of Kisselev (1932) who analysed net plankton from the Laptev Sea and found in the freshwater plume off the Lena Delta species such as *Pediastrum boryanum*, *P. biradiatum*, *P. duplex*, *Scenedesmus quadricauda* and *Botryococcus braunii* whereas only the occurrence of dominant freshwater phyto- and zooplankton was noted during plankton surveys in recent years (Heiskanen and Keck, 1996; Sorokin and Sorokin, 1996).

Therefore, we sampled plankton during the expedition to the estuaries of Ob and Yenisei for microscopical investigations. Net samples were taken from the near-surface waters along the salinity gradient to investigate the distribution of fossilizable aquatic and terrestrial palynomorphs in the freshwater layer.

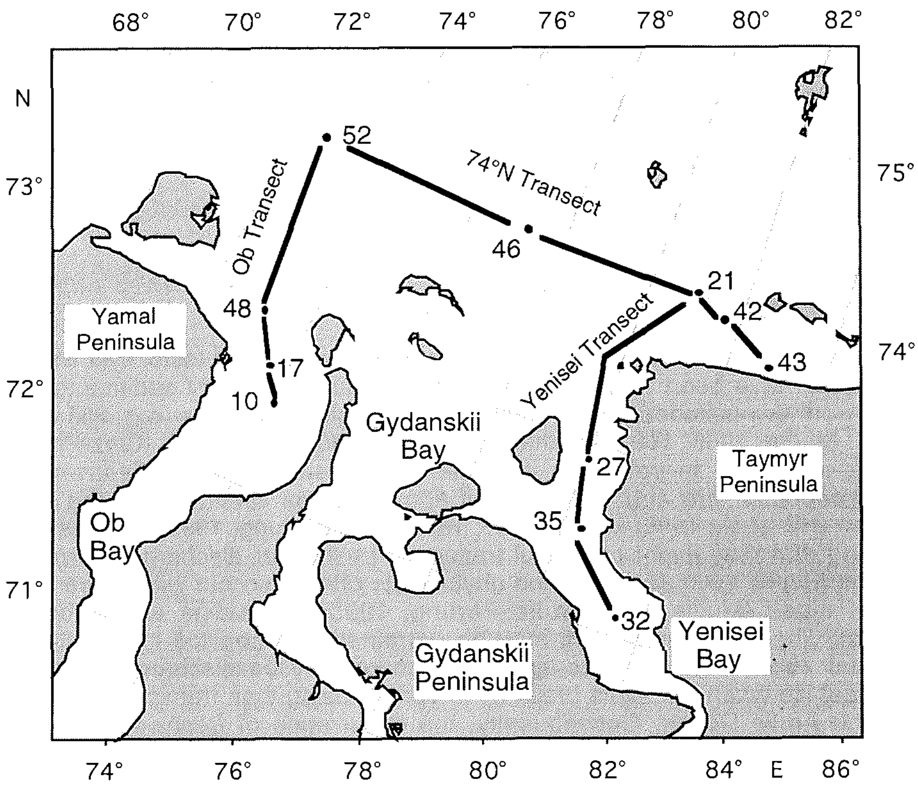

Fig. 1. Sample locations in the inner Kara Sea. Transects are indicated by lines.

Material and methods

During the expedition of RV "Akademik Boris Petrov" to the Kara Sea in September 1997, plankton samples were taken with an Apstein net from the upper 2 meters of surface waters along the Ob and Yenisei transects as well as the transect on 74°N (Boucsein and Siebold, 1998; Fig. 1; Table 1). A mesh size of 10µm was used because microscopical investigations on fossil particulate organic matter are usually conducted on size fractions larger than 6 to 10µm. All stations were located in the freshwater plume of the Ob and Yenisei rivers (Churun and Ivanov, 1998). The surface layer is composed of meteoric water (MW; riverine fresh water) or transformed meteoric water (TMW; mixture of riverine fresh water with saline surface water of the Kara Sea). Churun and Ivanov (1998) characterize MW as surface water having a salinity of less than 3.1 and 1.9psu in the Ob and Yenisei, respectively, and TMW having a salinity between 7.6 and 13.1psu and 5.7 to 11.8psu, respectively. The basic hydrophysical and hydrochemical data of the surface layer shown in Table 1 are from Churun and Ivanov (pers. comm.), Shpigun (1998) and Lukashin et al. (this volume).

The plankton was fixed in formaline (4%) immediately after sampling and stored under cool conditions until further examination (Boucsein and Siebold, 1998). In the laboratory the samples were washed with demineralised water to extract the formaline. A drop of the residue was mounted on a microscopic slide in glycerin gelatine and covered with a glass slip. The slides were analysed under the light microscope with 400x magnification using phase contrast and Nomarski interference contrast. To distinguish parautochthonous from reworked fossil POM, autofluorescene of individual particles is measured and the presence of chlorophyll in individual specimens recorded. Autofluorescence was determined with epifluorescene technique using blue light exication (wave length 450-490nm, ZEISS filter No. 9).

One slide per sample was completely examined and palynomorphs counted. Only semiquantitative estimates of palynomorph abundances are given in Table 1 because we did not take definite volumes of water. The bulk composition of the plankton was estimated in arbitrarily selected eye fields. It was not intended to give a full account of the plankton associations.

Table 1. Water column data and palynomorph content of surface water samples.

Transect	Station-No.	Date	Water type (a)	Temperature (a)	Salinity (a)	ph (b)	AlkT (b)	Suspension Concentration (mg/l) (c)	Diatoms	Dinoflagellates	Other Plankton	Pediastrum	P. angulosum	P. boryanum	P. duplex	P. kawraiskyi	P. simplex	Scenedesmus	S. quadricuda	Ciliates	Tintinnopsis spp.	Parafavella spp.	Pollen	Bisaccate Pollen
Ob	1	13.9	TMW	5.4	12.7	7.9	1625		C	D	A									R	X		R	
	48	22.9	TMW	4.8	13.5	7.8	1500	1.43	A	A	C	P		X	X					R	X		R	
	17	15.9	TMW	5.4	7.0	7.7	1100	7.36	D	C	C	C	X	X	X	X	X	P	X	C	X		R	
	10	14.9	MW	6.3	2.4	7.6	780	4.62	D	C	R	C	X	X	X		X	P	X	R	X		R	
Yenisei	21	17.9	TMW	5.7	15.3	7.9	1420	1.24	C	D	C	P		X						R	X	X	R	
	27	17.9	TMW	6.6	4.2	7.7	1040	1.89	C	A	C	P		X	X					C	X		R	
	35	19.9	MW	7.7	1.9	7.7*	990*	3.57*	D	A	A	C		X	X					C	X		C	
	32	18.9	MW	8.0	1.2	7.6	700	4.42	D	C	A	C		X	X					C	X		R	P
74°N	1	13.9	TMW	5.4	12.7	7.9	1625		C	D	A									R	X		R	
	18	16.9	TMW	5.4	11.0	7.8	1300		A	C	A									R	X		R	
	21	17.9	TMW	5.7	15.3	7.9	1420	1.24	C	D	C	P		X						R	X	X	R	
	42	20.9	TMW	5.9	14.9	7.1	1430		C	C	D									R	X		R	
	43	20.9	TMW	6.2	10.6	7.8	1360		C	D	C	P		X						R	X	X	R	

Abbreviations indicate: P = present; R= rare; C = common; A= abundant; D= dominant; X= species present.
(a) Churun & Ivanov (pers. comm.) * from station 30
(b) Shpigun (1998)
(c) Lukashin et al. (this volume)

Results

Bulk plankton composition
All samples usually are dominated by either diatoms or dinoflagellates, sometimes green and blue-green algae contribute significant amounts (Other plankton: Table 1). There is a gradient in plankton composition along the transects, diatoms are by far the dominant group in samples from the Ob and Yenisei bays, whereas dinoflagellates are more abundant in the inner Kara Sea. Because both groups have a low preservation potential, species have not been distinguished despite a strong variability in species composition. Polyakova (this volume) summarized results of several plankton surveys showing that freshwater species dominated diatom assemblages from the southeastern Kara Sea. Investigations on sediment trap material which was recovered close to our stations on the Yenisei transect in September 1993 (Lisitsyn et al., 1995) confirm these observations. Ciliates are the major zooplankton group in the net plankton. In particular empty tintinnid loricae are persisently present.

Fossilizable particulate organic matter
Particulate organic matter which has an excellent preservation potential contributes only small amounts to the entire net plankton and is mainly composed of aquatic palynomorphs (Table 1). Organic-walled phytoplankton is exclusively from freshwater to slightly brackish water habitats, whereas fossilizable marine palynomorphs such as dinoflagellate cysts are absent. *Pediastrum* is present in most samples but it is only rare to common in surface water with a salinity below 7psu where suspension concentrations are much higher than in the inner Kara Sea (Lukashin et al., this volume). *Pediastrum simplex* and *P. angulosum* are restricted to Ob Bay. Desmidiaceae are ocassionally present, while *Scenedesmus* was only recorded from the Ob Bay. This suggests that the Ob and Yenisei rivers might differ in their plankton populations. *Botryococcus* which may be quite abundant in the fossil record is absent.

The only zooplankton which have a certain preservation potential are tintinnid loricae belonging to the genera *Tintinnopsis* and *Parafavella*. In particular, *Tintinnopsis* which incorporates mineral particles into the lorica (Pierce and Turner, 1993) is common in surface waters from the southernmost parts of the transects, while few loricae of *Parafavella* spp. were found along the transect in the inner Kara Sea. Specimens were only assigned to genera because it has been shown that it is inadequate to use only lorica morphology for determination of species, e.g. in *Parafavella* (cf. Pierce and Turner, 1993).*Tintinnopsis* spp. and *Parafavella* spp. have been previously recorded from surface waters of the Kara and Laptev seas (e.g. Meunier, 1910; Echols and Fowler, 1973; Lisitzyn et al. 1995). Species of *Tintinnopsis* spp. may be considered indicators of low salinity surface water conditions because there are relatively abundant in the estuaries of Ob and Yenisei and in surface sediments off the Lena Delta (cf. Echols and Fowler, 1973), and the Lena River (Sorokin and Sorokin, 1996). *Parafavella* spp. apparently requires relatively high sea-surface salinities (cf. Meunier, 1910; Echols and Fowler, 1973). However, it must be kept in mind that loricae can be transported over long distances (Pierce and Turner, 1993).

Suprisingly, terrigenous palynomorphs are relatively rare. Pollen are continuously present. Bisaccate pollen and plant debris only occur at station 32 in Yenisei Bay.

Fluorescence colour was used to distinguish fresh from reworked particulate organic matter. The green to yellow-green autofluorescene colours indicated that all aquatic palynomorphs were not reworked. About 10 to 30% of all *Pediastrum* and *Scenedesmus* specimens contained chlorophyll indicating that the specimens were alive when they were transported. Most empty coenobia of *Pediastrum* have open reproduction openings indicating that they reproduced. This might have happened in the low salinity water mass from which they were sampled (Table 1) because at least *P. boryanum* and *P. kawraiskyi* may reproduce at salinities as high as 6 to 8psu (Matthiessen and Brenner, 1996). We do not know whether the tintinnids recorded lived in the surface waters because we found only their empty loricae. However, this could be an artifact of sampling because it has been observed that tintinnids abandon their loricae when collected with plankton nets (Pierce and Turner, 1993).

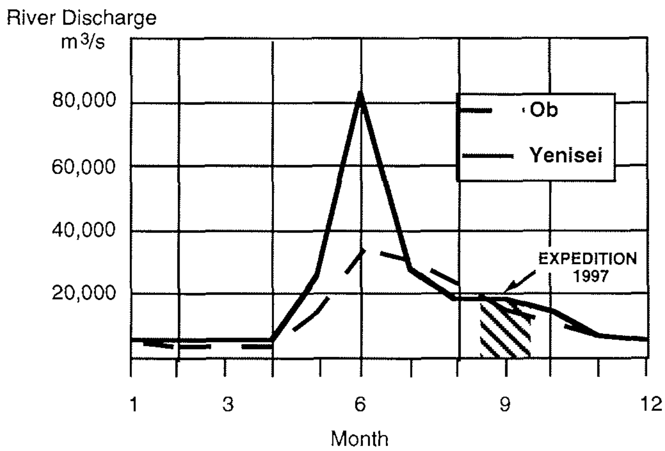

Fig. 2. Annual mean discharge of the Ob and Yenisei rivers into the Kara Sea based on ca. 50 years of monitoring (from Pfirman et al., 1995). The period of the Kara Sea expedition is indicated by hatching.

Discussion and conclusions

The low amounts of terrestrial palynomorphs, almost exclusively pollen, is a striking feature in our surface water samples. This may be caused by the sampling technique because the samples (>10µm) comprise only a small fraction of the bulk suspension load. In September 1997 the suspension consisted of clays to silty clays with only minor amounts of silt larger than 5µm (< 3%) (Lukashin et al., this volume). The clay and fine silt fractions might be dominated by terrestrial particulate organic detritus as suggested from maceral analysis of bulk surface sediments (Boucsein et al., this volume). Therefore, the grain size fraction containing the bulk of the terrestrial organic matter might not be sampled with the plankton net.

However, the clays and silty clays may comprise also large amounts of freshwater algae because palynomorphs have a low density and may therefore have an equivalent grain size of fine silt and clays despite the fact that palynomorphs are usually larger than 20µm. If they had a much higher density, then they would have been sedimented in the upper reaches of both rivers, probably in the deltas of Ob and Yenisei. Terrestrial palynomorphs have approximately the same density and are at least as large as freshwater algae. If they were present in the surface water suspension during the sampling period, they must have been found in our samples as well. However, these terrestrial palynomorphs except for pollen were in particular absent in surface waters from the inner bays which contained maximum concentrations of suspension (Lukashin et al., this volume). Therefore, we assume that larger particulate organic matter of terrestrial origin did not play an important role in September 1997.

The samples taken in September 1997 reflect the late summer situation when the discharge of freshwater is already approaching winter levels (Fig. 2) and relatively small amounts of suspended matter is supplied by Ob and Yenisei (Gordeev et al., 1996). The preservable particulate organic matter in the surface waters is clearly of aquatic origin with freshwater algae dominating. A marine signal having a definite preservation potential (except for diatoms) is absent. The fluorescence colours of the freshwater algae suggest that they are just transported into the environment and not reworked.

The apparent discrepancies between the composition of the suspension load and the surface sediments (Boucsein et al., this volume; Matthiessen, this volume) may be explained by a strong seasonality in terrestrial and aquatic palynomorph influx and/or a selective degradation of planktic organisms. The terrestrial signal in surface sediments probably reflects the major seasonal discharge events of freshwater and terrigenous sediments in June, whereas our samples reflect a predominant influx of aquatic production which may have a lower preservation potential (e.g. dinoflagellates, diatoms). Therefore, water column samples should be taken in particular from the freshwater plume in spring (Fig. 2). Sediment traps are probably the most powerful tool to reveal the annual cycle of POM discharge. This will also allow to investigate the seasonal cycle of aquatic organic matter sedimentation (local production vs. transported marine and riverine production) which is influenced by the strong short-term changes in surface water conditions (e.g. Churun and Ivanov, 1998).

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ORGANIC GEOCHEMISTRY

STABLE ISOTOPES IN MODERN WATER AND BIVALVE SAMPLES FROM THE SOUTHERN KARA SEA

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Introduction

The Kara Sea covers a shelf area, where on a large scale water masses of very different characteristics and history are mixing. The saline and comparatively warm Atlantic Water mixes with salt-free river water of temperatures, which are changing through the seasons, and (in the north) with low-saline, cold Arctic surface water. Formation and melting of sea ice, which extract and supply freshwater, are complicating the hydrographic situation. The formation of high-saline water masses ("shelf brines") from freezing of sea water is important for the renewal of the Arctic Intermediate Water. This water mass leaves the Arctic Ocean through the Fram Strait to the Greenland and Iceland seas, where the renewal of North Atlantic Deep Water is initiated, as part of the global oceanic Conveyor Belt.

While the general features of the major water masses are well known, our knowledge of the isotopic characteristics of the river water outflow, the mixing processes in the estuaries and the southern Kara Sea, and the reflection of the isotopic characteristics in calcareous benthic shells is still scarce. In this paper we present first results of a pilot study on samples obtained in late summer 1997 inside and north of the estuaries of the rivers Ob and Yenisei. Preliminary data include the amount of dissolved organic carbon (DIC) and the carbon isotope composition ($\delta^{13}C$) of selected water samples and the carbon and oxygen ($\delta^{18}O$) isotope composition of bivalves, genus *Yoldiella* sp., from selected sediment surface samples.

Materials and methods

The samples were obtained during the 28th cruise of RV "Akademik Boris Petrov" in the second half of September 1997 (Matthiessen and Stepanets, 1998). The sampling area was confined to 72 to 74°N of latitude and 72 to 84°E of longitude, covering the northern parts of the Gulf of Ob and Yenisei with water depths about 10 to 15 m and northward the open sea with water depths up to 56 m (Fig. 1). Water samples were taken as soon as possible after the rosette sampler had returned to the ship's deck to avoid loss of CO_2 and exchange with atmospheric CO_2. Water was filled slowly into 100 ml ground glass bottles and 0.2 ml $HgCl_2$ were added to stop biological activity. Bottles were carefully sealed with a glass stopper applying a trace of silicon grease (Erlenkeuser et al., 1995) and stored at ca. 4°C.

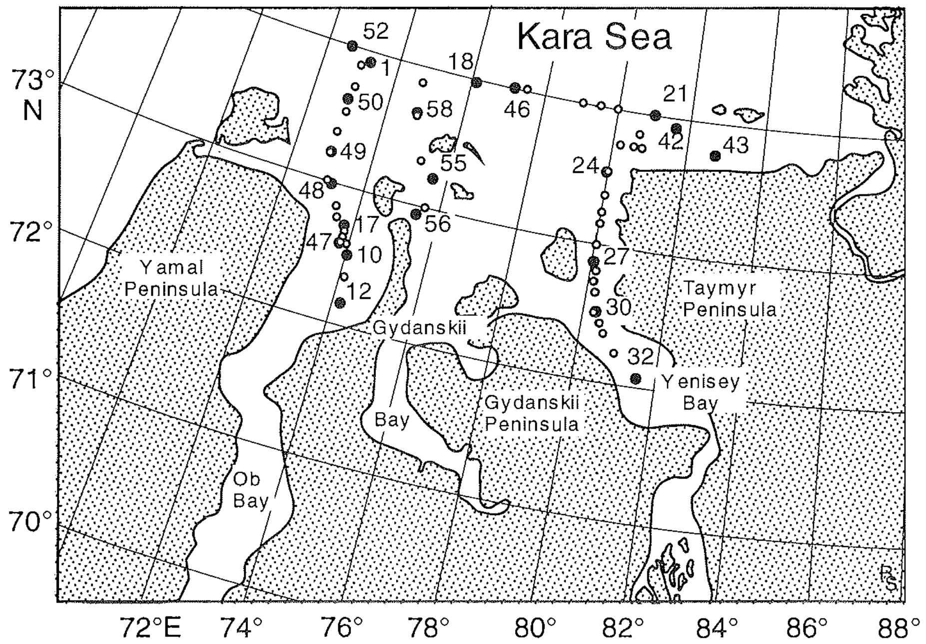

Fig. 1: Sampling locations in the Kara Sea. Labelled, black dots indicate locations of samples analyzed for this pilot study.

Prior to isotope analysis suspended particulates were removed on a 0.2 µm membrane filter using 4.5 grade nitrogen as pressurizing agent. Filtered water was collected in a tightly attached 100 ml reagent bottle with ground neck, thoroughly flushed before with nitrogen and protected against back-diffusion from the atmosphere by a capillary venting outlet. Sample net weight was determined by weighing (±0.01 g) the full and emptied flask.

Water samples were processed on the automated Kiel DICI-II device for CO_2 extraction from water samples, which is operated on-line to a Finnigan-MAT Delta E mass spectrometer. Both instruments are operated under the Kiel 'Control-It' MAC OS software (Cordt and Erlenkeuser, 1994). The basical principles of CO_2 extraction follow the off-line procedure applied earlier (Erlenkeuser et al., 1995).

The sample bottle was attached to one port (of 8) of the DICI device, with the interior of the port bulb being kept under a gentle outflow of nitrogen during the procedure. Sample water is acidified with 3 ml 30% phosphoric acid and CO_2 gas stripped with a total of 1200 ml of 4.5 grade nitrogen carrier gas supplied at a rate of 100 ml/min. Gasflow and stripping gas pressure slightly above normal are controlled electronically. CO_2 gas (plus water vapour) is trapped from the carrier at -194°C under vacuum, and is destilled from water residues into a temperature-controlled cold trap/reference-volume equipped with a 0.2 % class 0 to 1000 mbar solid state pressure gauge to quantify CO_2 yield. CO_2 gas is directly inlet to the mass spectrometer. Excess CO_2 may be collected in a glas ampoule and flame sealed for later AMS ^{14}C-analysis.

The relative external error for DIC is ±0.5% for 50 to 100 ml samples of usual waters with DIC about 1 to 2 mMol/kg. Accepting lower DIC performance, samples down to 5 ml (100 μMol CO_2) may be processed for isotope analysis. Blanks are less than 0.2 μMol CO_2, and replicate stripping releases less than 0.5 μMol CO_2.

Isotope composition is given in the usual δ notation. Calibration is based on the NBS 20 carbonate isotope standard. External error including sample processing and isotope analysis is ±0.04‰ on the δ scale.

Sediment surface samples were taken with multi corers (diameter 6 cm) and giant box corers (50 x 50 cm surface). Slices of 2 cm thickness were taken from 2-3 multicore tubes per station. From a 10 x 10 cm area of each box core surface, the upper 2.0-2.5 cm were sampled. All samples were fixed in a bengal-rose-methane solution to stain living specimens and stop biologic activity. Samples were stored at ca. 4°C. Details of sampling procedures aboard RV "Akademik Boris Petrov" are given in Matthiessen and Stepanets (1998).

In the GEOMAR sedimentology laboratory, samples were freeze-dried and rinsed through a 63 μm mesh with deionized water. After drying at 40°C, stained specimens of *Yoldiella* sp. were hand-picked from the >63 μm fraction. Depending on size, whole shells - 1 shell each - or parts were taken for isotope analysis. Parts were broken off from the ventral part of larger shells under the microscope using a cutting edge for mechanical forcing. This simple technique produced differently sized fragments of unknown seasonal coverage and can only provide a first access to the benthic isotope signature of the Kara Sea environment.

The shells or shell fragments were transferred to the glass ware reaction tubes for CO_2 preparation and broken therein with a glass rod for easy acid access. The carbonates were reacted with phosphoric acid (100%) at 73°C under vacuum in the automated KIEL-I carbonate preparation unit on-line fitted to a Finnigan-MAT 251 spectrometer. Isotopic composition is given in the usual δ notation and is calibrated to the PDB scale by means of the NBS 20 carbonate isotope standard. External errors are ±0.08‰ and ±0.05‰ for $\delta^{18}O$ and $\delta^{13}C$, respectively.

Results and discussion

The waters of the southern Kara Sea are strongly influenced by the freshwater discharged in the south by the rivers Ob, Gydanskii, and Yenisei, and reveal a pronounced haline stratification at all latitudes (Churun and Ivanov, 1998): While the upper 15 m of the water column in the working area have salinities between 2 and 22‰ (depending on location), values below 20 m generally are >30‰. This stratification is also reflected in the amount of dissolved inorganic carbon (DIC) and in the stable carbon isotope composition of the DIC (Fig. 2). There is a good correlation between salinity and DIC (Fig. 3; Fig. 4): The analyzed deeper, saline waters have DIC content of 1.8-2.3 mMol/kg, while brackish waters above show 0.8-1.8 mMol/kg. DIC and salinity measurements have been performed on different subsamples from a station and effective water depths occasionally appear to be slightly different. This may have offset the relation of DIC and salinity when a pronounced halocline was sampled (c.f. Fig. 4).

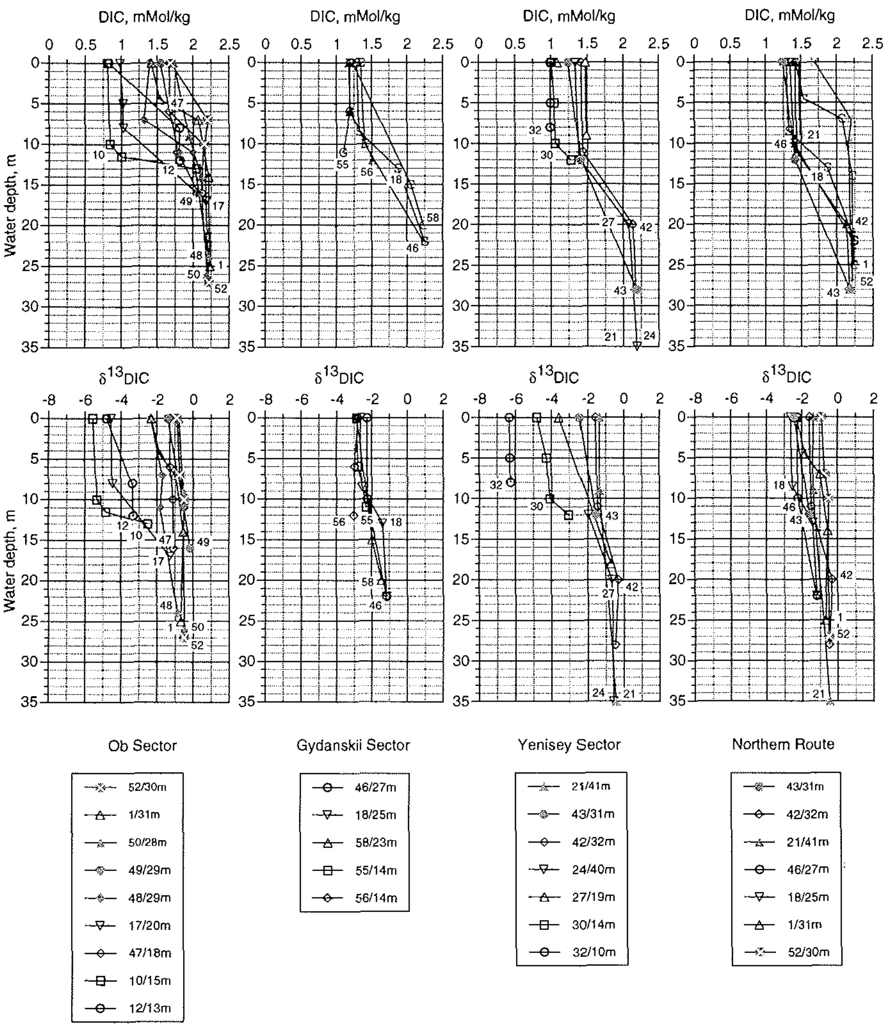

Fig. 2: Distribution of DIC and $\delta^{13}C$ of DIC with water depth, arranged for 3 meridional sectors and a northern transect in the Kara Sea. Station number and total water depth are given in the legend.

The carbon isotope composition (^{13}C / ^{12}C ratio, as $\delta^{13}C$) of the DIC in the analyzed water samples ranges between 0.8 and 2.2‰. The primary marine component, defined as Atlantic water from the Norwegian Sea (below 30 m water depth), typically has a DIC content of 2.1 mMol/kg and $\delta^{13}C$ values closely grouping around +1.1‰PDB (Erlenkeuser, 1995). On a regional scale, deep waters in the northwestern part of the research area reveal significantly lower $^{13}C/^{12}C$-ratios about $\delta^{13}C$= -0,5‰ (Fig. 2) at basically the same DIC level (2.1 to 2.3 mMol/kg). On the other hand, the freshwater source, characterized by the low DIC-content (0.65 mMol/kg; Fig. 4), is given a $\delta^{13}C$ value of -7‰ PDB as was extrapolated from the measured results by models of $\delta^{13}C$ vs. DIC or $\delta^{13}C$ vs. salinity (Fig. 5). Stable isotope studies on the carbon balance of these environments hence must consider the effect of water mass composition.

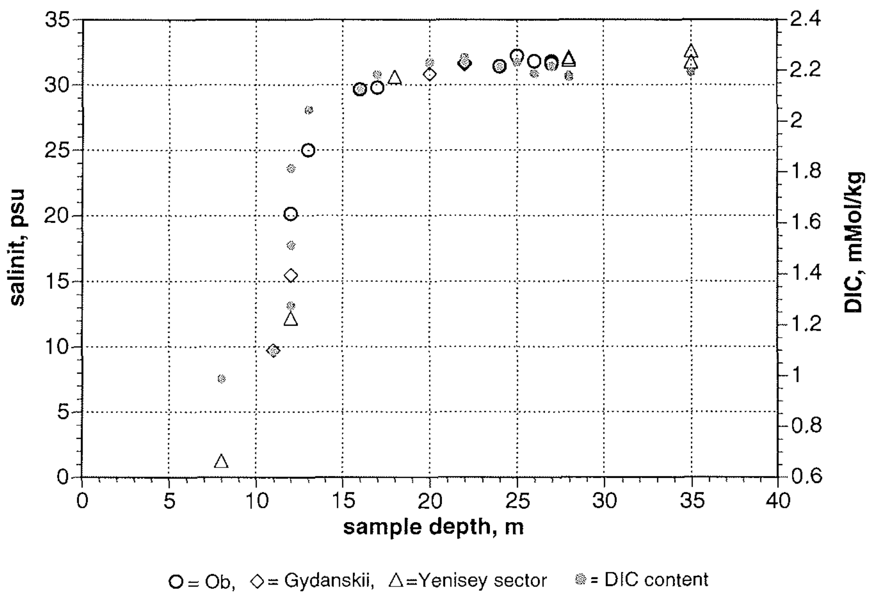

Fig. 3: Variation of salinity and DIC content with sampling depth, shown for the bottom water samples.

Presuming purely physical mixing and a two source constellation, mixing fresh and marine waters predicts a non-linear relation between $\delta^{13}C$ and DIC as shown in Fig. 5. Such model seems to be verified by the surface waters (x-labelled data). The deep waters, however, appear to deviate in particular in the high DIC range, i.e. at higher salinity. Interestingly, deviations also appear for particular stations or sample depths. A systematic effect shows up for stations from the inner estuaries, such as the southern station 32 from the Yenisei Estuary, for the deeper waters of station 12 (Ob), and for deep waters of station 10 (Ob), and is possibly related at some stations to the halocline (station 48, outer Ob Estuary; 56, outer Gydanskii Estuary; 58 and 18, northern shelf). These results are thought to reflect the effect of remineralization processes on the DIC system of the bottom waters: The degradation of organic detritus, exported to the bottom from planktonic production or input from terrestrial sources by the rivers, increases the DIC content through the release of ^{13}C-depleted, i.e. isotopically light organogenic CO_2.

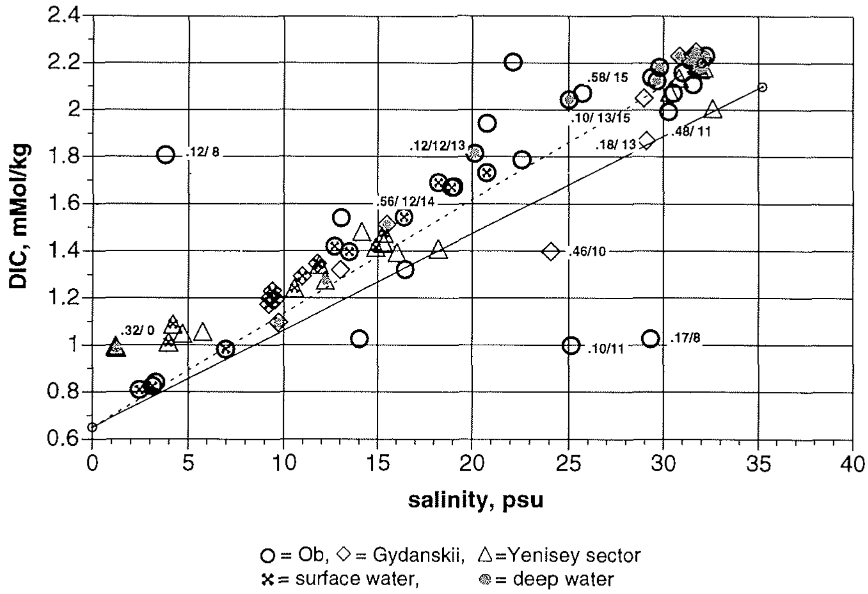

Fig. 4: DIC vs. salinity. Lines indicate a regional (dotted) and a 'global' (solid) two source mixing model for comparison with the data (c.f. text). Respective end points are indicated.

A regional two source mixing model, applying appropriate parameters for the fresh water and the regional marine source provides a reasonable fit (Fig. 5b, dotted line). A global model, in the sense that it refers to marine source characteristics as shown by Norwegian Sea water, clearly is not sufficient. DIC content exceeds this 'global' model (Fig. 4), and $\delta^{13}C$ is depleted (Fig. 5b, solid line). This probably emphasizes the possible isotope history of these waters on the drift eastward, in particular on the Barents Sea shelf west of the Kara Sea, or could reflect a significant contribution of remineralized organic carbon such as from terrestrial sources (river input?).

An alternative mixing model using salinity instead of DIC as the mixing variable with otherwise unchanged parameters shows a different quality of fit (Fig. 5a). This also indicates that biological processes of CO_2 consumption and release have affected the DIC and accordingly have impacted on the carbon balance of the Kara Sea. Also, part of the offset could be due to variations of salinity by sea ice formation and melting. These aspects need further studies to be quantified.

The varying freshwater significance with depth is also shown in the stable oxygen isotope composition of shell carbonate of the bivalve *Yoldiella* sp. Bivalves of this genus are assumed to build their carbonate shells in equilibrium or constant disequilibrium with the ambient water. The average oxygen isotope composition (^{18}O / ^{16}O ratio as $\delta^{18}O$) of Siberian river water may be as low as -21‰ (Östlund and Hut, 1984). Values of 16.3 and 17.5‰ have been reported for the Ob and Yenisei rivers (Brezgunov et al., 1983), and -19‰ were found - by extrapolation with salinity - in the Laptev Sea for Lena

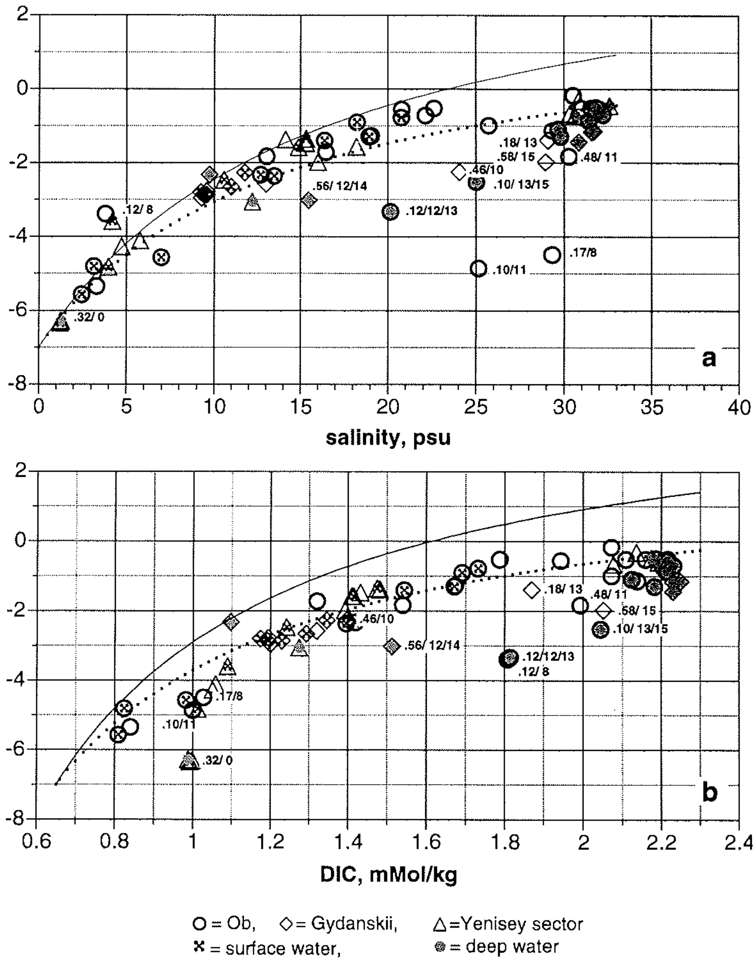

Fig. 5: Variation of $\delta^{13}C$ of DIC with salinity (a) and DIC (b). Dotted line shows a regional, solid line shows a 'global' two source mixing model (c.f. text). Inserted numbers give station no./ sampling depth/ total water depth, if sample is the deepest of the station.

river water (Erlenkeuser, unpubl.). On the other hand, marine (Norwegian Sea) water has a $\delta^{18}O$ value of +0.3‰ (Erlenkeuser, 1992; Schlosser et al., 1994; Bauch, 1995). From these values, bivalves from shallow, strongly freshwater influenced water depths can be expected to show low $\delta^{18}O$ values, wheras those from deeper living species should be higher in ^{18}O. Hypothetical $\delta^{18}O$ values for the bivalves were calculated according to Shackleton's (1974) paleotemperature equation from the temperature/salinity data for the deepest sampling at the respective station (data of L.K. Shpigun in Matthiessen and Stepanets, 1998). Although there is some evidence for a linear relationship between measured $\delta^{18}O$ values of *Yoldiella* sp. and the expected oxygen isotope composition (Fig. 6a), deviations become evident for shallow and

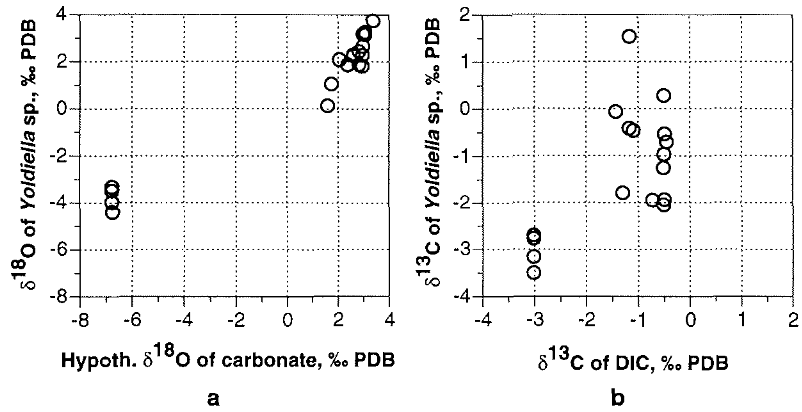

Fig. 6: Measured isotopic composition of *Yoldiella* sp., collected alive. a) $\delta^{18}O$ versus hypothetical isotopic equilibrium calculated from temperature and salinity data of the bottom waters. b) $\delta^{13}C$ compared with the dissolved inorganic carbon isotopes.

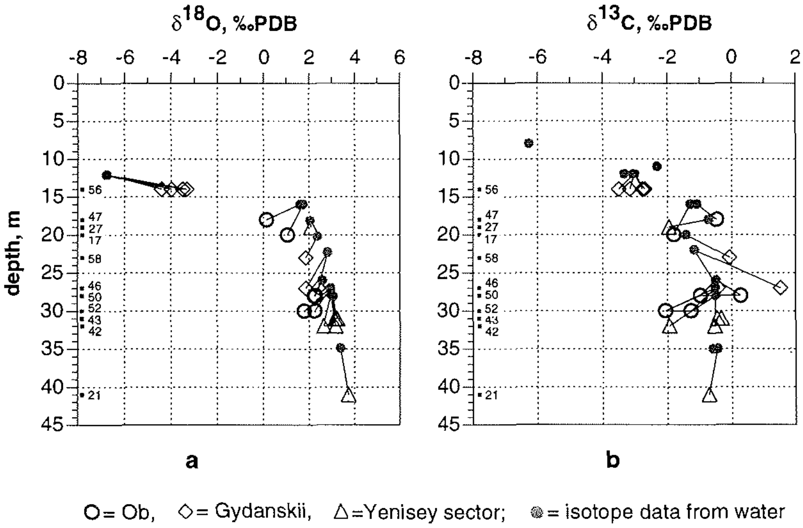

Fig. 7: Distribution with water depth of $\delta^{18}O$ (a) and $\delta^{13}C$ (b) of shells of *Yoldiella* sp. collected alive. Hypothetical isotopic equilibrium values of $\delta^{18}O$ calculated from temperature and salinity, and $\delta^{13}C$ of the dissolved inorganic carbon isotopes are shown for the deepest water sampled at the respective station. Numbers denote stations.

intermediate depths (Fig. 7a). These depths are subject to significant seasonal variations of the physical conditions and the related isotopic situation. The seasonal history is integrated in the shells of the benthic faunas during their lifetime, whereas the analyzed water samples provide the momentary status, here the autumn well after the annual maximum of the fresh-water discharge. Thus, the observed differences probably result from the different time resolution of the sample types compared. However, in general the relation of $\delta^{18}O$ vs. depth (Fig. 8) is very similar to that for the Laptev Sea (Erlenkeuser et al., in press) and could provide access to a measure of paleo-water depth.

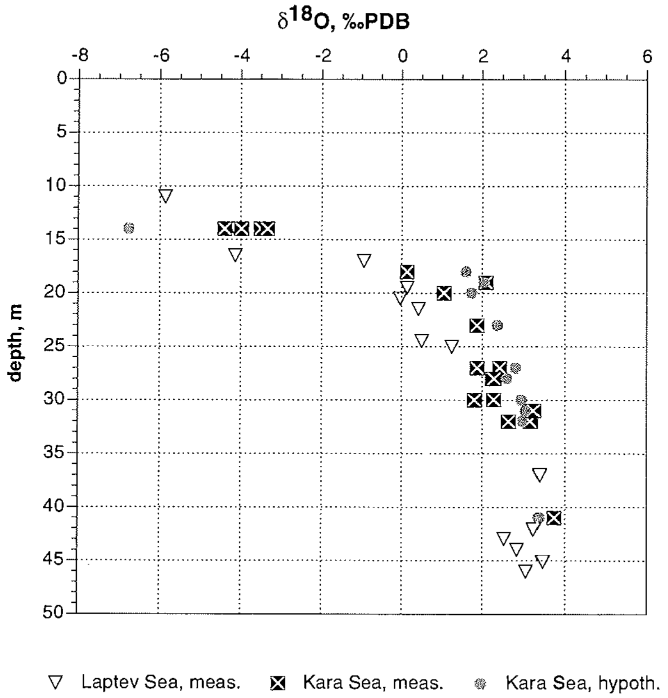

Fig. 8: $\delta^{18}O$ values of the bivalve *Yoldiella* sp., collected alive from the Siberian shelf of Laptev Sea and Kara Sea, and $\delta^{18}O$ of hypothetical carbonate precipitated in isotopic equilibrium, as calculated from temperature and salinity data of contemporaneous Kara Sea water samples.

The range of the stable carbon isotope composition of *Yoldiella* (Fig. 7b) is about the same as shown by the deep water DIC from the respective stations. In particular, both the marine end member on a northern station (21) and low saline shallower stations in the south (17, 56) as an approach to the riverine end member are met and reveal isotopic consistency with the water data. In general, the stable isotope composition of the biogenic benthic carbonates apparently provides a fair reflection of the local physico-chemical environment, although some data points do show some offset from isotopic equilibrium of water and carbonate shells (Fig. 7). Since the offset is stronger at greater water depths, a possible explanation could be a stronger admixture of ^{13}C-depleted fresh water during the main calcification season of the bivalves (summer?).

Clearly, the effects of the interfering seasonalities of the fresh water impact and the organic biogeochemical processes deserve a more detailed study. This may help to understand and quantify the characteristic of the carbon balance in this large, fluviatile controlled shelf area, also for paleoecological applications through benthic carbonates and their isotopic information, and helps investigate the potential of the wide Kara shelf sea as a possible site of carbon transfer and export to the world ocean.

Acknowledgements

We thank B. Finkenberger for her careful work of sampling water and sediments onboard RV "Akademik Boris Petrov". T. Dahl and P. Körner prepared the sediment samples. We are very much obliged to H. H. Cordt, Leibniz-Lab., who has developed the Kiel DICI-II device and its software and took care of the measuring routines. He also surveyed the Kiel I carbonate system. We thank H. Gier and H. Heckt, Leibniz-Lab., for operating the isotope analytical facilities.

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ISOTOPE GEOCHEMISTRY OF PARTICULATE ORGANIC CARBON IN THE YENISEI ESTUARY: SOURCES AND REGULARITIES OF DISTRIBUTION

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Introduction

The Kara Sea receives more than one third of the total fresh water discharge into the Arctic Basin and the river Yenisei has the greatest run-off (1,98 $*10^4$ m^3/s, Degens et al., 1991; Dai and Martin, 1995). Detailed information on sources and composition of organic material delivered by this river will improve our understanding of the organic material transported onto the shelf area and further to the central Arctic Ocean which is eventually buried in the sediments. However, few studies have been devoted to the chemical oceanography in this area, and the Kara Sea remains one of the most poorly studied Arctic shelf areas. This holds true especially for different elements of the carbon cycle in the water column. Particulate organic carbon is an integral part of the biogeochemical carbon cycle in the marine environment. It is intermediate between the biological source of organic matter and the sedimentary organic pool, being a transport vehicle of organic matter to the bottom (Kodina et al., 1994, 1996).

Our experimental approach in the present study consists of organic carbon isotope analysis of the particulate load coupled with the study of stable isotope ratios in dissolved inorganic carbon (DIC) which is a carbon source for primary bioproducers. Rock Eval pyrolysis was used to get an independent evidence for genesis and source of organic matter.

Study area

Investigations were carried out during the 28th cruise of RV "Akademik Boris Petrov" in September-October 1997. The investigation area is located between 72° and 74° N, and 74° and 86° E. The transect River Yenisei - adjacent Kara Sea (hereafter referred to as "Yenisei-Sea" transect) extends from the southern estuary to the Kara Sea and comprises 7 stations, with a nominal spacing of about 30-40 nautical miles. Figure 1 shows the locations of the stations. Four stations (St. 32, 30, 27, 24) are representative of the Yenisei estuarine area, St. 21 is located in the adjacent part of the open sea, St. 42 is located on the pathway of the eastern branch of the Yenisei current and St. 43 is located nearshore of the Taimyr Peninsula where some small rivers discharge into the Kara Sea. The transect was sampled within a period of 4 days (17-20 September), and may be considered therefore as quasi-synoptic.

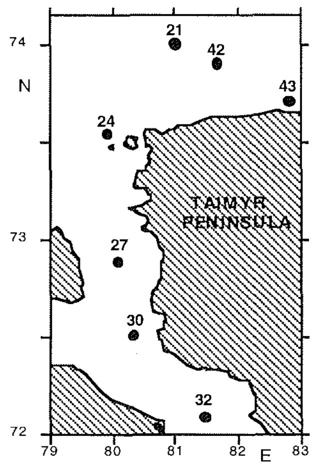

Fig. 1. Location of stations at "Yenisei-Sea" transect, carried out in September 1997 during the 28th cruise RV "Akademik Boris Petrov".

Temperature and salinity were measured on 23 vertical profiles along the transect using a conductivity-temperature-depth (CTD)-profiler (OTS-PROBE Serie 3). The water column in the study area is stratified with a strong pycnocline between the surface and bottom waters (Churun and Ivanov, 1998).

Sampling and methods

Water sampling was carried out by using a Rosette sampler equipped with Nansen bottles of 1,8 l each. Samples of particulate organic matter for determination of POC isotope composition were collected by pumping water samples (1,5-3 l) onto precombusted (450° C, 6 hours) Whatman GF/F fiberglass filters (diameter 47 mm). For POC isotope analysis, 1/8-1/4 part of each filter (organic carbon content more than 0,1mg) was used. A specimen was treated with $HCl_{conc.}$ to remove carbonate carbon if present. Organic carbon isotope ratios were measured after reacting the sample with CuO in a quartz reactor at 1000° C. The CO_2 was collected on cold traps and analysed with a Varian Mat 230 mass spectrometer. Results are reported as per mil deviation from the PDB standard. The standard deviation of the procedure did not exceed 0.2‰ PDB.

The stable isotope ratio of dissolved inorganic carbon (DIC) was determined in water samples of 50 ml taken immediately after Rosette deployment. The samples were treated on ship to precipitate DIC as $BaCO_3$. Blood flasks of 250 ml containing a centrifuge tube for $Ba(OH)_2$ were used. The flasks were evacuated, $Ba(OH)_2$ solution injected and the water sample acidified with syringes through the rubber plug of the flask. The acidified samples were heated to 70°C to evolve CO_2 completely. $BaCO_3$ precipitates were centrifuged, washed and dried. The bulk precipitate from each flask was used as a single specimen for routine carbonate carbon isotope measurements in the institute's laboratory. The standard deviation of the isotope analysis including all preparative procedures was smaller than 0.7‰.

Table 1. Hydrological parameters, particulate organic and dissolved inorganic carbon isotope composition, and abundances of particulate and dissolved organic carbon throughout the "Yenisei-Sea" transect.

St.	Depth m	S psu [Churun & Ivanov,1998]	AlkT meq/l [Shpigun,1998]	$\delta^{13}C_{POC}$ ‰ PDB	$\delta^{13}C_{DIC}$ ‰ PDB	C_{POC} µg/l	C_{DOC} mg/l
43	0	10.56	1360	-26.4	-6.7	134	-
	20	18.22	1550	-25.1	-4.1	-	-
	28	32.13	2180	-24.5	-4.0	247	-
42	0	14.88	1430	-25.6	-4.2	276	-
	11	15.30	1520	-25.1	-3.8	310	-
	20	30.82	2070	-24.9	-	204	-
	28	31.92	2200	-25.7	-2.8	208	-
21	0	14.77	1420	-25.4	-6.2	265	4.2
	10	17.45	1550	-26.4	-4.5	263	3.9
	15	30.13	2060	-24.6	-	221	3.2
	35	32.58	2250	-25.4	-2.9	178	3.6
24	0	11.87	1380	-26.7	-6.0	294	4.3
	12	16.01	1540	-26.1	-5.3	181	4.5
	20	30.32	1940	-25.0	-	176	2.5
	35	31.76	2280	-26.1	-2.4	397	2.7
27	0	4.20	1040	-27.3	-7.6	146	4.4
	8	7.99	1140	-26.6	-6.5	377	5.3
	18	23.00	2140	-27.4	-3.5	265	2.9
30	0	3.97	990	-27.8	-8.2	221	-
	5	4.70	1060	-27.9	-8.6	122	-
	10	5.77	1160	-27.6	-	186	-
	13	12.19	1280	-27.4	-5.4	-	-
32	0	1.22	700	-28.2	-8.3	248	-
	5	1.21	750	-27.6	-7.3	191	-
	8	1.27	1000	-28.8	-	157	-

POC concentration was determined after "wet" combustion of a glass-fiber filter aliquot with a mixture of bichromate - concentrated sulfuric acid (800°C, 2h) and the evolved CO_2 volume was measured coulometrically. The standard deviation is ca. 5% (Ljutsarev and Chubarov, 1994).

DOC concentrations were determined analogously in water samples poisoned with $HgCl_2$ after sampling and stored in a refrigerator until analysis.

For isotope analysis, two phytoplankton samples were kindly collected by Dr. J. Matthiessen (AWI) on the transit from the Yenisei Estuary to the Ob transect along parallel 74° N at longitude 77-73°E and 73-72° E. About 1500 l of surface water was filtered through a plankton net with mesh size of 10 µm. The samples were poisoned with $HgCl_2$ on board and stored frozen. The phytoplankton consisted mainly of diatoms.

Rock-Eval II pyrolysis was performed on selected samples from the uppermost sediment layers of the multi corer in the standard temperature range from 300 to 600°C with a heating rate of 25°/min.

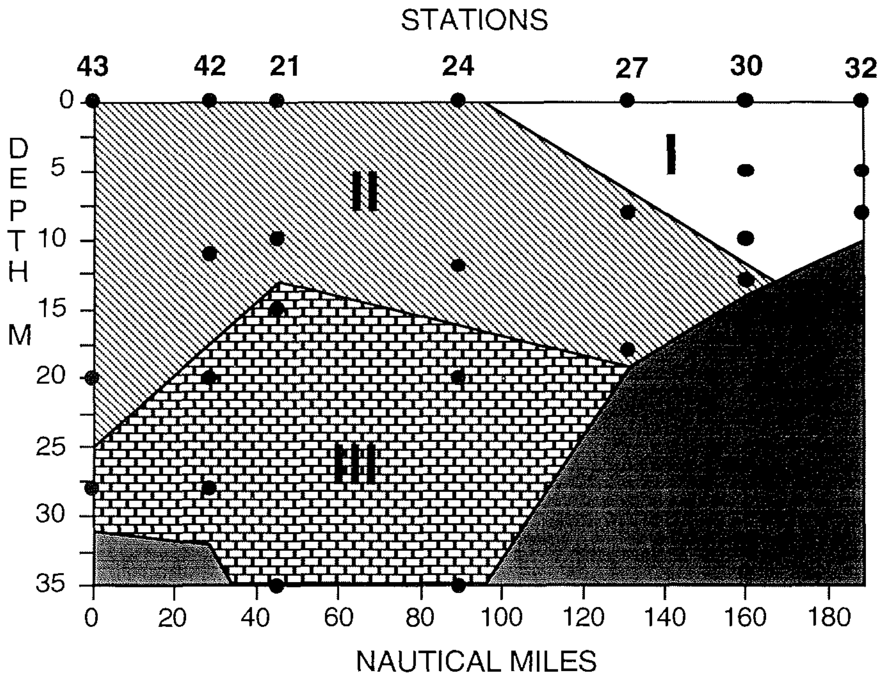

Fig. 2. Distribution of three water zones in the "Yenisei-Sea" transect with distinct POC isotope composition.
- Zone I ("fresh" water), S<8 psu, $\delta^{13}C_{POC}$=-27,9±0,4 ‰,
- Zone II (mixing of fresh and sea water), 8<S<28 psu, $\delta^{13}C_{POC}$=-26,2±0,8 ‰,
- Zone III ("marine" water), S>28 psu, $\delta^{13}C_{POC}$=-25,2±0,5 ‰.

Results and Discussion

In the present paper, new experimental data on the stable carbon isotope composition of particulate organic and dissolved inorganic carbon in the Yenisei Estuary are presented. The data on POC and DIC, abundance of POC and DOC together with main hydrochemical parameters are listed in Table 1. Evaluating the isotope composition of POC and DIC on the background of the stratified water masses revealed some essential features in the POC isotope distribution pattern and clarified the origin of the particulate material in the water column of the estuary.

Hydrological zonality of the stratified water

The hydrophysical water column structure in the study area is typical of estuaries with sharp vertical and horizontal density gradients (e.g. Fedorov, 1983).

Based on the salinity, the water column in the study area can be divided into three zones. The vertical structure of the water column along the transect "Yenisei-Kara Sea" is schematically shown in Figure 2.

In the southern part of the Yenisei Bay (St. 30, 32) the water column in zone I consists practically of fresh and brackish "river" water with a salinity S<8 psu from the surface to the bottom. The thickness of the fresh water layer decreases sharply from the "river" end member to the north and disappears at the latitude of about 73°30' N (St. 24, 39). Proportions of intruding "marine" and mixing water (zones II and III), on the contrary, are progressively increasing from St. 30 to St. 21. Dense and cold "marine" bottom water characterize the zone III with S>28 psu. The two contrasting water masses are separated by an intermediate "mixing" water mass forming zone II (8<S<28 psu).

Table 2. Average values of the main characteristical geochemical parameters for the 3 general water zones of the transect "Yenisei-Sea".

Zone	S psu	Alk_T meq/l	$\delta^{13}C_{POC}$ ‰ PDB	$\delta^{13}C_{DIC}$ ‰ PDB	C_{POC} µg/l	C_{DOC} mg/l
I	<8	957	-27.9	-7.6	182	4.4
II	8-28	1483	-26.2	-5.2	262	4.2
III	>28	2140	-25.2	-3.0	233	3.0

Dissolved Inorganic Carbon (DIC) isotope composition in water masses of different salinity

In the present study the isotope composition of DIC was determined at each hydrochemical station for three horizons: subsurface, bottom and intermediate - corresponding to the three water masses of different salinity described above. The results are listed in Table 1. In order to clarify the DIC isotope distribution pattern throughout the area, it is appropriate to consider the means for each of the three water masses (zones I-III). The average isotope composition and concentrations of POC and DIC are presented in Table 2.

There is a positive correlation between Alk_T and salinity throughout the investigation area both vertically and spatially (Tables 1, 2; Shpigun, 1998). A similar trend for DIC isotope composition was observed, with enrichment of ^{13}C when salinity and alkalinity increase and thus the isotopically heaviest carbon being in the "marine" water mass about -2.4‰ and an average value of -3.0‰. For the "fresh" water zone I the average $\delta^{13}C$ -value is of -7.6‰ and minimal -8.6‰. It corresponds well with the DIC isotope ratios of terrestrial fresh water with typical values of -9 to -14‰ which is opposite to the marine and oceanic environment with an average value of surface water of 0-2‰ (Galimov, 1985; Kroopnick,1985).This relationship is shown in the study area both vertically and spatially. The correlation coefficient for DIC isotope distribution versus water salinity is as high as r=0.8. DIC isotope composition is believed to be intrinsic for the distinctive water masses.

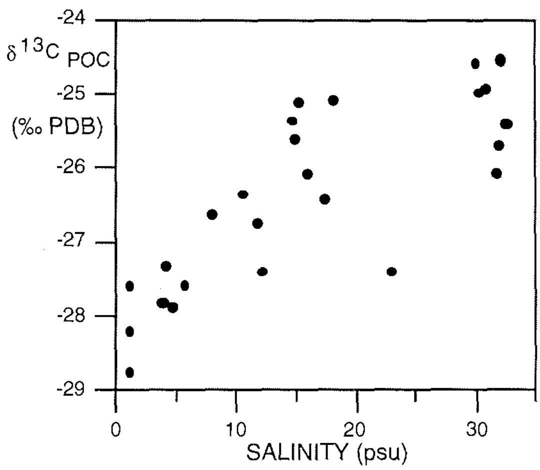

Fig. 3. Distribution pattern of POC isotope composition ($\delta^{13}C_{POC}$, PDB) against salinity (S, psu) in the study area.

POC isotope distribution in water masses of different salinity

Table 1 shows that the POC $\delta^{13}C$-values range from -28,8 to -24,5‰. Plotting the values against salinities (Fig. 3) demonstrates a high correlation between both parameters (r=0.8), as in case of DIC isotope composition. However, there is no correlation between POC concentration and salinity (r=0.2).

The POC isotope ratio of the most fresh "river" water (Zone I) is, on average -27.9 ± 0,4‰ (Fig. 2). In the "mixed" water (Zone II), organic carbon of the suspended load is characterized by elevated mean values of $\delta^{13}C$= -26.2± 0.8‰. The "marine" water of maximal salinity (Zone III) contains the isotopically most heavy organic carbon of -25.2±0.5‰. The mean values for each water mass are statistically significant and do not overlap each other.

Clearly, the isotopically lightest organic carbon (-28.8‰) was measured in the fresh water (S=1.2 psu), whereas the heaviest $\delta^{13}C$-isotopes (-24.5‰) were observed in the intruded marine bottom water of maximal salinity (S=32 psu). The intermediate water mass (Zone II) resulted from mixing of the first two water masses and POC isotope composition is a mixture of both sources. Correspondingly, the POC isotope composition is intermediate (-26.2 ±0.8‰).

The spatial distribution of $\delta^{13}C_{POC}$ shows the same regularity as the vertical one. The distribution versus salinity of the subsurface water layer (depth of 0-1 m) along the transect "Yenisei-Kara Sea" is illustrated in Figure 4. The ^{13}C-isotope values generally run parallel with water salinity, increasing from lower values in the southern part of the transect gradually from -28.2 to -25.4‰ in the northern estuary and open sea. A drop in salinity at St. 43 is parallel to a decrease of the ^{13}C concentrations in DIC and particulate load.

Therefore, the variations of the POC isotope composition are correlating with the variations of salinity and DIC isotope composition in the study area, thus being an inherited feature of the specified water mass.

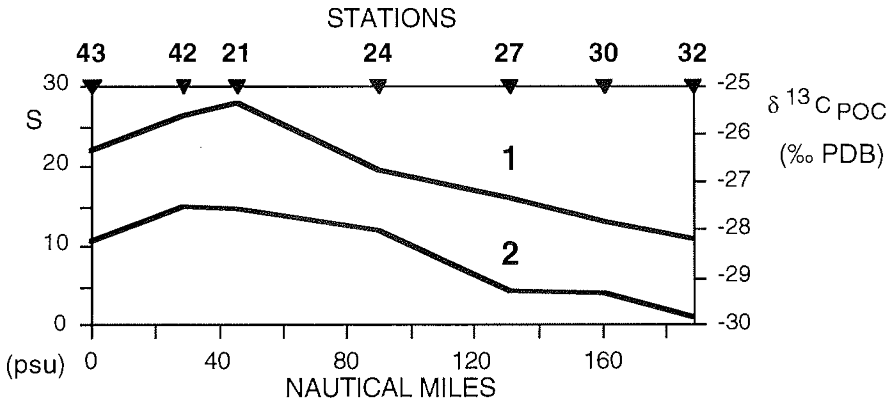

Fig. 4. Distribution of $\delta^{13}C_{POC}$ (‰) (curve "1") and S (psu) (curve "2") in the subsurface water layer (depth 0-1 m) along the "Yenisei-Sea" transect.

On the nature of particulate organic matter

In principle, organic carbon from several sources may contribute to the total particulate load in the Yenisei Estuary:

-terrestrial (land-derived) biomass and its geochemical derivatives, exemplified by soil humus, collected by the river from the huge (2,58 $*10^6$ km^2) catchment area (taiga and tundra) (Degens et al., 1991);
-planktonic biomass, produced in the fresh river and brackish mixing water of variable salinity;
-planktic detritus, advected in marine water of high salinity and flowing landward into the estuary;
-organic particles, resulting from DOC flocculation due to mixing of saline and fresh water;
-resuspension of bottom sediments by bottom currents and tidal flows.

The range of the POC isotope variation observed in the area (-28,8 to -24,5‰) suggests that each of the sources mentioned above contributed to the POC inventory of the Yenisei Estuary with a dominance of the isotopically light, river-borne sources.

Interpretation of the organic carbon isotope data for the estuarine area is complicated by the heterogeneity of river-borne organic matter on one side, and the wide variability of the carbon source (DIC) isotope composition in the area, on the other side. An elevated bioproductivity in the oligotrophic Kara Sea was measured precisely in the areas affected by river discharge due to nutrient supply to the sea and higher temperature (Vedernikov et al., 1994). Taking into account the characteristic feature of Arctic shelf seas, that bioproductivity and salinity are reversely related, it is reasonable to consider organic matter in the estuary as a mixture of land-derived "recycled" matter and "fresh" matter of planktonic origin, produced in the river fresh water and estuarine brackish water. In this case, it is important to know the isotope composition of the end members, namely plankton and wood biomass, being the most widespread source of terrestrial biomass (Hedges and Oades, 1997).

Table 3. Organic carbon isotope composition and pyrolytic parameters of the bulk plankton samples and woody plant remains from bottom sediments of the estuarine zone.

Sample	Water salinity psu	$\delta^{13}C_{org}$ ‰	C_{org} % (TOC)	HI mgHC/ gC_{org}	OI $mgCO_2$/ gC_{org}	HI/OI
plankton 74°N, 73-72°E	11.70	-26.6	25.80	257	30	8.6
plankton 74°N, 77-73°E	18.20	-25.9	20.30	383	52	7.4
autochtonous detritus* 76°55'N 69°13'E	31.00	-22.4	2.50	450	152	3.0
autochtonous detritus* 76°58'N 70°05'E	~31	-22.6	1.87	464	119	4.0
wood remain St.32	1.27	-26.5	15.60	80	91	0.9
wood remain St.24	11.80	-26.6	20.70	59	149	0.4
wood remain St.27	4.20	-26.3	-	-	-	-

*The data are from St. 57 and 58, 22th cruise of RV"Akademik Boris Petrov" (Galimov et al., 1996).

Organic carbon isotope composition, coupled with the pyrolytic characteristics of the two possible POC sources in the estuary, are presented in Table 3. The samples are woody plant remains found in sediments at stations 24, 27, and 32, phytoplankton samples collected in the the open sea at 74°N and surface sediments from the upwelling area north of Novaja Zemlja (Galimov et al., 1996). All wood remains are characterized by uniform isotope composition of about -26.5‰ (Table 3), typical for land-derived biomass (Galimov,1985). The isotope composition of the brackish water plankton samples are similar (-26.6 and -25.9‰), related to a water salinity of 11.8 and 18.2psu, respectively. The higher isotope values of around -22‰ are apparently characteristic for "normal" marine bioproduction. It is evident that the organic carbon isotope composition of phytoplankton is defined by the DIC isotope composition which in turn relates directly to water salinity.

The low POC ^{13}C values in the upper estuarine area (-27 to -28‰) are believed to correspond well with a substantial fresh water plankton contribution to the organic carbon balance in the local water and reflect an impact of the isotopically light river-borne carbon source. In contrast, the isotopically heaviest POC samples with ^{13}C values > -25‰, examplified by St. 43 (-24,5‰) or St. 21 (-24,6‰) are believed to be influenced by the advection of marine water of high salinity with inherent "normal" marine plankton with $\delta^{13}C$ values of - 22 to -23‰.

Terrestrial and planktic matter in the estuarine zone can sometimes not be distinguished by carbon isotopes. However, biochemistry of land plants and planktonic biomass differ significantly from each other: the first is rich in woody components, namely lignin, cellulose, and hemicellulose and poor in hydrogen-rich compounds such as lipids and proteins, which are characteristic of plankton (Anderson, 1995). Consequently, pyrolytic data for the two types of organic matter are different which is clearly demonstrated by the data listed in Table 3. The high HI-values (HI>200) and low OI-values (OI<100) with HI/OI>1 are strongly pronounced characteristics of planktonic biomass, whereas the low HI (HI<100), elevated OI (OI>100) and very low HI/OI <1 values are characteristic for terrestrial material. Pyrolysis data of the "fluffy" layer of sediments recovered with the multi corer may serve as an additional index to distinguish the two types of sedimentary organic matter in the marine environment influenced by river outflow. HI-values ranging from 200 to 300 mg HC/g TOC were recorded at some stations.

Sedimentary organic matter, resuspended by bottom currents and tidal flow, may serve as a potential source of POC as well. Despite the evident absence of any correlation between the POC concentrations and salinity, an obvious trend of POC increase is seen when salinity increases to more than 8 psu (Table 1,2). Nevertheless, we suppose the flocculation of dissolved organic matter to be a most probable reason for the positive correlation of POC concentration and salinity.

We have only a restricted data set of DOC concentrations in the Yenisei Estuary and adjacent open sea (Table 1). The absolute values range from 2.7 to 5.3 mg/l and are higher than DOC concentration in the central Arctic Ocean (Wheeler et al., 1996). A good inverse correlation (r=0.8) was found between DOC concentration and salinity (Table 2). The averaged DOC and POC concentrations in the three water masses of different salinity enable us to assume that formation of new particles occurs in the estuarine area due to flocculation of dissolved organic molecules at the contact of fresh and saline waters. The process is particularly effective at salinity 5-8 psu as is shown by natural observations and laboratory experiments (Artemjev and Shapiro, 1987; Lisitzyn, 1994). However, the new-formed particles seem to be hardly detectable on the basis of their carbon isotope composition because of the similarity of the bulk POC and DOC isotope composition (Eadie et al., 1978).

All data presented above demonstrate the existence of two substantial sources of particulate matter in the Yenisei estuarine area, namely terrigenous organic matter with a carbon isotope composition of about -26‰ and autochtonous plankton-derived detritus with an isotope composition ranging from -22 to -30‰, depending on the nature and isotope composition of dissolved inorganic carbon. However, the isotope composition of different carbon sources is related directly to water salinity.

Conclusions

Particulate organic carbon isotope composition ranging from -28,8 to -24,5‰ coupled with data of Rock eval pyrolysis of organic matter demonstrate the heterogeneity of particulate load in the Yenisei Estuary. The bulk of the POC in the Yenisei estuarine zone is composed of relatively inert terrestrial, land-derived organic matter (-26.5‰) and "fresh" organic matter made up of river-borne plankton (-<28‰) as well as estuarine brackish water planktonic biomass (>- 28‰). Isotopically heavy normal marine plankton (-22‰) advected in marine water of high salinity should not be excluded as a possible component of the particulate load. The flocculation of dissolved organic compounds might be an additional POC source in the estuary.

Spatial and vertical distribution pattern of POC isotope composition is controlled by the DIC isotope composition in the stratified water column of the estuary. There is a direct correlation between the local water salinity and the isotopic composition of the carbon cycle elements.

$^{13}C/^{12}C$ ratios of particulate organic and dissolved inorganic carbon are supposed to be characteristic features for the water masses of different salinity and different origin.

The direct relation between water salinity and isotope composition of organic and inorganic elements of the carbon cycle might have important consequences: it enables to predict the nature (source) of organic particulate matter in any locality of an estuarine area. Such information are basic to balance different genetic types of organic carbon in the marine environment.

Acknowledgements

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DISTRIBUTION OF DISSOLVED ORGANIC CARBON DURING ESTUARINE MIXING IN THE SOUTHERN KARA SEA

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Introduction

Dissolved organic matter in the ocean is recognized as a very large pool of reactive organic carbon potentially influencing the global carbon cycle on time scales of a 1000 - 10000 years. Reports on dissolved organic carbon (DOC) in the Arctic Ocean are somehow inconsistent with respect to DOC concentrations as well as origin. Due to the Mediterranean nature and the large amounts of river discharge, Arctic DOM can be expected to carry a strong terrestrial signal. However, the fate of terrestrial organic matter in the ocean has recently been recognized as contradictory itself (Hedges et al., 1997). The annual input of terrestrial organic matter to the global ocean is enough to replace the oceanic DOM pool in less than 3000 years (Deuser, 1988), however, only trace amounts of terrestrial derived organic matter can be detected in oceanic samples. Either our estimates are wrong or a so far uncharacterized removal mechanism is at work. More detailed studies of the land - ocean interface are in demand to solve this lingering puzzle.

Ob and Yenisei, two of the three largest Arctic rivers enter the Kara Sea and contribute more than 40 % of river water and about 35 % of total organic carbon discharge to the Arctic Ocean (Telang et al., 1991). This immense river input and the extended shelf area make the Kara Sea an ideal place to study terrestrial-derived DOM transformation processes during estuarine mixing. The behavior of DOM during estuarine mixing has been studied in the past with results indicating a range from conservative mixing to 60 % losses of DOM. Most recent studies, including Siberian rivers (Mantoura and Woodward, 1983; Lisitsyn, 1995; Cauwet and Sidorov, 1996; de Souza Sierra et al., 1997; Cai et al., 1998), however, indicate conservative mixing behavior of DOM with 1 - 5 % losses of DOM in the low salinity range (0-3‰). The degree of DOM loss appears to be related to the chemical composition of riverine DOM. Hydrophobic compounds (humic acids) tend to be lost preferentially during the estuarine mixing process (Thurman, 1985). The role of colloidal organic matter has also been discussed in this context but only few data are available at this time. Colloids are thought to be important transport agents for contaminants and their fate during estuarine mixing needs to be elucidated.

In this paper we present preliminary results on DOM distribution in the southern Kara Sea during a cruise onboard the RV "Akademik Boris Petrov" in August/September 1997. The two rivers, Ob and Yenisei were sampled along salinity gradients to investigate the distribution of DOC, high molecular weight (HMW) DOM, as well as humic substances. More detailed information on the elemental, isotopic, and molecular composition of Kara Sea DOM will be presented elsewhere as soon as available.

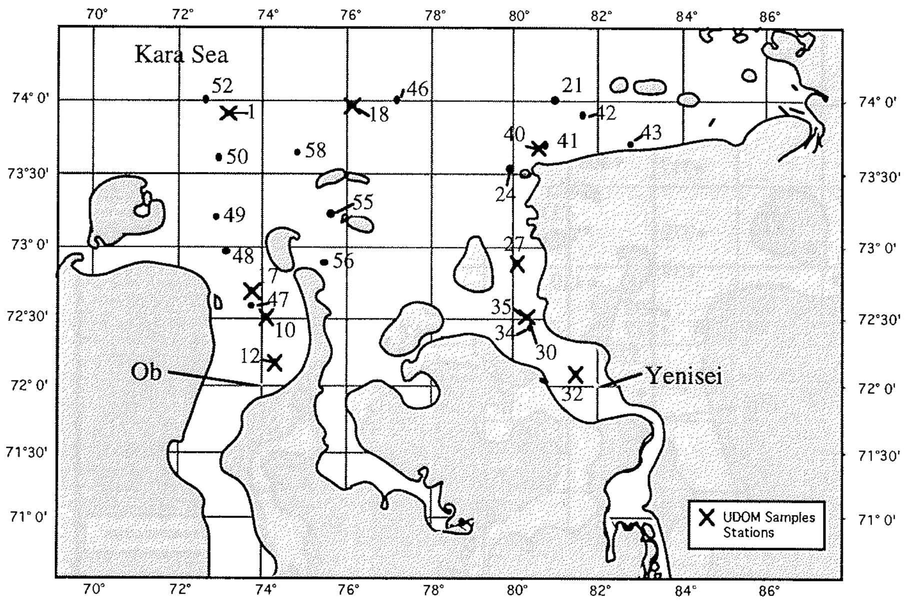

Fig. 1a. Map of the southern Kara Sea with Ob and Yenisei estuaries, showing (a) the sampling sites for dissolved organic carbon (DOC; dots) and ultrafiltration samples (crosses) and (b) the actual DOC concentrations during the sampling period in September 1997.

Material and Methods

Samples were collected in the Ob and Yenisei estuaries, roughly between 72° N and 74° N and between 72° E and 84° E as indicated in Figure 1a. Surface water samples for DOC analyses were taken at 25 stations using Niskin bottles mounted onto a rosette sampler. Large volume (200l) water samples for ultrafiltration and humic substance extractions were collected with a large volume sampler (Batomat 200l) at 12 stations. For more information on the sampling procedures see Steffen et al. (1998).

DOC Analyses
Samples (20 ml) for DOC analyses were taken from the Niskin bottles, and transferred to the laboratory in acid rinsed polypropylene bottles. Samples were immediately filtered through precombusted Whatman G/FF filters, and stored in sealed glass ampoules at -20°C until analyses. All glassware was precombusted at 500°C for 6 h. DOC analyses were performed using the high temperature combustion method and a Shimadzu TOC 5000 analyzer (Benner and Strom, 1993; Benner and Hedges, 1993).

Ultrafiltration
The large volume samples were immediately filtered through 3 µm and 0.2 µm polycarbonate Nuclepore filters in a sequential manner. Samples were stored in acid rinsed polypropylene and high density polyethylene containers at about 4°C onboard the ship until arrival at the home port. Water samples were ultrafiltered within 5 weeks of sampling. No significant changes in DOC con-

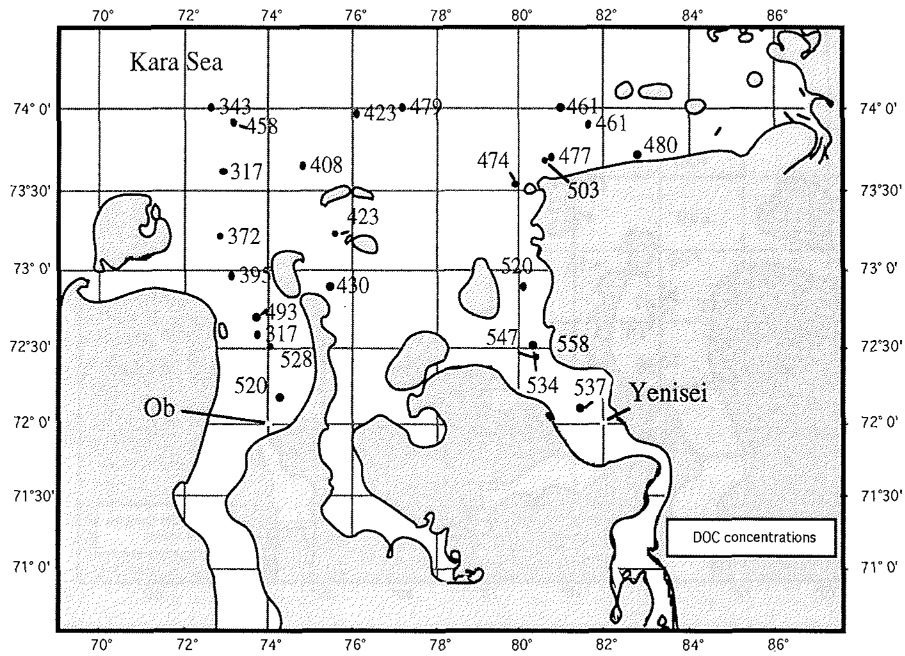

Fig. 1b. Concentrations of dissolved organic carbon (DOC).

centrations were observed during storage of the samples. Ultrafiltrations were performed using an Amicon Proflux M30 tangential-flow ultrafiltration system equipped with Teflon coated valves. We used 2 stacked spiral-wound polysulfone filter cartridges with a molecular weight cut off of 1 kDa (1 nm). Samples (145 - 183 l) were concentrated down to about 1,2 l yielding an average concentration factor of 140. After the ultrafiltration the concentrate was diafiltered with 15 - 20 L MQ water in order to remove inorganic salts. The DOM concentrate, also referred to as ultrafiltered DOM (UDOM) or high molecular weight (HMW) DOM includes parts of the colloidal fraction of DOM (0.01 - 0.2 µm). For further details on the ultrafiltration process and cleaning procedures see Benner et al. (1997).

Extraction of humic substances

For each sample, 70 liters from the 0.2 micron filtrate (see above) were acidified to pH 2 with hydrochloric acid and passed through a glass columm filled with XAD-8 resin (Thurman and Malcolm, 1981). Sorbed hydrophobic substances, herein defined as humic substances, were eluted from the resin with alkaline solution (NaOH).

Results and Discussion

DOC distribution

Concentrations of DOC ranged from 320 - 530 µM C in the Ob Estuary and from 460 - 560 µMC in the Yenisei Estuary (Fig. 1b). These values are very similar to DOC concentrations in the Laptev Sea reported recently for the same

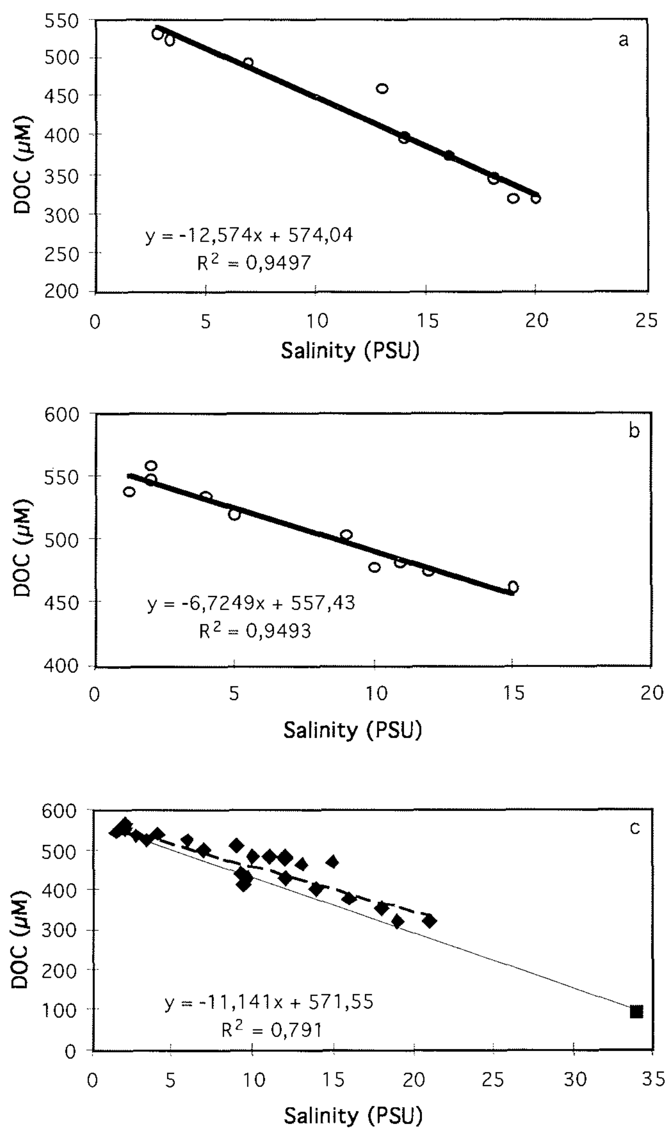

Fig. 2. Distribution of dissolved organic carbon (DOC) across a salinity gradient in the Ob (a) and the Yenisei (b) with regression line and equation showing. Panel c shows the pooled data for both rivers including intermediate stations. The broken line indicates the regression through all data points (diamonds) and the solid line indicates the conservative mixing line assuming a marine endmember DOC concentration of 93 µM C as explained in the text.

season (Cauwet and Sidorov, 1996). The main features of DOC values as presented in Figure 1b are the slightly higher carbon concentrations in the Yenisei and the much higher DOC values in the eastern Kara Sea. The lower values in the west are most likely a result of changing hydrodynamic conditions during the cruise as indicated by big temporal changes of salinities (Shpigun, 1998). DOC values in the Yenisei area compare well with Ob-values during the first Ob-sampling period (stations 1-17), but values are much lower during the second Ob-sampling period (stations 47-52), a week later. This indicates that a water mass with very distinct salinity and DOC values entered the Ob Estuary between the two sampling periods.

The DOC distribution across the salinity gradient indicates largely conservative mixing of DOM between 2 and 20‰ (Fig. 2). The major difference between the Ob and Yenisei transects is the steeper slope of the conservative mixing line (Fig. 2a, b) in the Ob Estuary, indicating that waters from the Ob were mixed faster and with a different marine endmember water mass than Yenisei waters. Unfortunately, we were not able to sample pure endmembers and therefore we can not conclusively show that conservative mixing of DOM occurred across the entire salinity gradient.

In order to increase our resolution for the sampled salinity range, we pooled all the collected data from the Kara Sea (Fig. 2c). A regression through those data returns a fairly strong relationship (Fig. 2c) and allows us to calculate the DOC concentration for the theoretical marine endmember. Assuming a salinity of 34‰, the marine endmember has a calculated DOC concentration of about 200 μM C. This is much higher than one would expect from samples with such a high salinity, but interestingly it is almost the same value as reported by Cauwet and Sidorov (1996) for the Laptev Sea marine endmember. There are three possible explanations for such high theoretical DOC concentrations in the marine endmember. First, our DOC measurements are wrong, which is unlikely since we measured DOC with 2 independent methods. Second, the marine endmember has in fact high DOC concentrations. Such high DOC concentrations at salinities above 34‰ have not been measured in slope waters of the Arctic Ocean and we would therefore need a DOM enrichment mechanism to explain the elevated values. Third, there is an additional source for DOM on the shelf besides the DOM discharged by the two rivers. At this point we favor the last explanation and suspect DOM release from terrestrial-derived particulate organic matter (POM). Losses of POM have recently been indicated for the Amazon Estuary (Keil et al., 1997). If we assume a more reasonable DOC value for the marine endmember, like 93 μM C, as reported for the northwestern Laptev Sea at 34 ‰ (Kattner et al., in press), the DOM surplus becomes more obvious (Fig. 2c). Besides DOM release from POM and sediments, the DOM surplus could also come from phytoplankton production. Initial data on the carbon isotopic composition of Kara Sea UDOM show depleted δ^{13}C values, typically around -28‰, and C/N ratios above 40 (Amon and Benner, in prep.), indicating that marine phytoplankton is an unlikely source for the surplus DOM. The sediments in the Kara Sea receive large quantities of terrestrial derived particulate organic material which could leach DOM with the observed δ^{13}C and C/N signal.

Distribution of UDOM

UDOM samples were taken across the 2 salinity gradients between 1.5 and 12.7 ‰ (Fig. 1a). A significant fraction (49 - 72%) of DOM was isolated by ultrafiltration (Table 1) with higher recoveries at lower salinities. Interestingly, the Yenisei Estuary samples appear to have a greater portion of DOM as HMW DOM or UDOM (58-72%) than the Ob Estuary samples (49-57%). The reported recoveries are typical for riverine and estuarine DOM samples (Amon and Benner, 1996). The distribution of UDOM across the observed salinity range is shown in Figure 3, indicating that UDOM largely mixes in a conservative manner. The UDOM distribution confirms previous studies, in that DOM of terrestrial origin is of higher molecular weight than marine DOM (Amon and Benner, 1996). The number of UDOM samples (n=4) in each of the river-shelf transects is low and make interpretation very speculative. It appears, however, that concentrations of UDOM behave as conservative as bulk DOC.

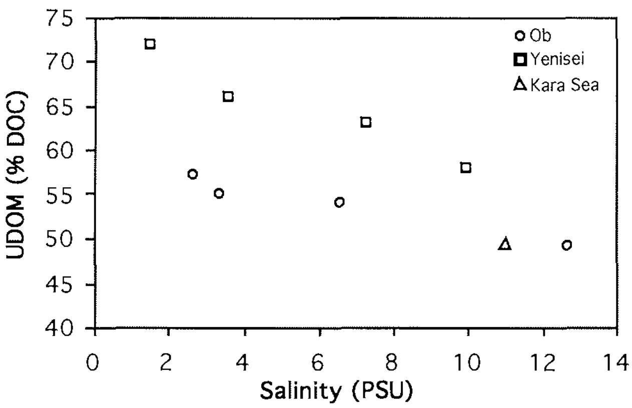

Fig. 3. Distribution of dissolved organic matter concentrated by ultrafiltration (UDOM) across a salinity gradient in the Kara Sea. UDOM is presented as UDOM-carbon relative to total DOC.

Distribution of humic substances

So far, we quantified the DOC in the humics recovered (Table 1). Between 1.5 and 15 per mil salinity humics account for about 30 % of total DOC. At two high salinity end member stations (31.5 and 32 per mil salinity) humics account for 25 and 23% respectively of the DOC. Overall the recovery appears relatively low and further studies will have to substantiate this result. As a global figure, one would typically expect 50% or more (Malcolm, 1990; Spitzy and Leenheer, 1991). However, in this study we were not able to sample the freshwater end member below 2 permil salinity, where already significant losses can occur due to flocculation.

The preliminary results presented herein show promise in respect to our ability to characterize DOM dynamics in the Kara Sea, however, they also indicate limitations to our interpretations and the need for more detailed studies in this very important area. In particular, we need to extent our sampling effort to the low salinity (0-3‰) as well as the high salinity (>22‰) regions. Many recent studies (Cai et al., 1998: Cauwet and Sidorov; 1996; Lisitsyn, 1995; Souza Sierra et al., 1997) demonstrated the importance of the low salinity region for DOM losses. In order to proof our hypothesis, that DOM concentrations are in excess of the values expected from pure mixing of river and slope waters, we need to sample the higher salinity regions of the shelf and the slope. Only with those samples and more detailed information on the chemical composition of

DOM will we be able to determine the responsible factors for elevated DOM concentrations in Arctic shelf areas and the fate of terrestrial DOM in the Arctic basins. If our hypothesis proves to be true, export of terrestrial-derived DOM from the Eurasian shelves could have been severely underestimated.

Table 1: Distribution of dissolved organic matter in the Kara Sea. High molecular weight DOM = UDOM (>1 kDa) versus humic substances (XAD 8).

Station	Latitude N	Longitude E	Salinity ‰	DOC µM C	UDOM %	HS %
1	73°54'38	73°10'59	12.7	458	49	27.4
10	72°30'10	74°04'51	2.7	528	57	34.4
12	72°10'13	74°17'37	3.4	520	55	32.8
17	72°41'19	73°43'50	6.6	493	54	29.0
18	73°57'42	76°08'19	11.0	423	49	
21	74°00'02	81°00'27	15.0	433		31.0
24	73°32'04	79°55'16	32.0	150		23.0
27	72°53'21	80°05'33	7.3	520	63	33.0
32	72°05'35	81°28'52	1.5	537	72	34.0
34	72°25'50	80°24'26	1.9	442		30.0
35	72°30'31	80°19'43	3.6	534	66	
40	73°40'51	80°36'39	10.0	503	58	
46	73°59'51	77°12'14	31.5	158		25.0

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NITROGENOUS ORGANIC MATTER IN SURFACE SEDIMENTS IN THE ESTUARIES OF THE OB AND YENISEI RIVERS

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The Arctic basin represents the catch basin for material transported by rivers draining a significant part of the Eurasian continent and North America. The bulk of this material stems from the Russian rivers Pechora, Ob, Yenisei and the Lena (Telang et al., 1991). Although these inputs have a significant impact on the ecology of the Arctic basin, information on the pattern of their dispersal and distribution in the adjacent coastal seas is scarce (Kassens et al., 1998). This paper presents preliminary results of analyses of organic matter in surface sediments collected from the estuaries of the Yenisei and Ob rivers and from the Kara Sea. The results are discussed in terms of the sources of the organic matter.

Material and Methods

The sediment samples were collected during the Kara Sea Expedition of the RV "Akademik Boris Petrov" in 1997 (Fig. 1). In all, 21 sediment cores were collected with a multicorer ("MUC"). Each core was sampled at 5 cm intervals. Additional samples were taken from individual lithological units. Surface sediments were analyzed for their bulk components such as carbonate and biogenic silica (opal) as well as organic carbon, nitrogen, amino acids and hexosamines (Haake et al., 1993).

Total carbon and total nitrogen were measured on a Carlo Erba Nitrogen Analyzer 1500. Duplicate analyses led to an average standard deviation of ±0.02% for nitrogen and ±0.05 % for carbon. Organic carbon (C_{org}) was calculated by subtracting carbonate-carbon from total carbon. C/N ratios were calculated from weight percentages of organic carbon and total nitrogen. Total organic matter was calculated by multiplying organic carbon by 1.8 (Müller et al., 1986). Carbonate was determined conductometrically with a Wösthoff Carmhograph 6. Standard deviation was ±1%. Biogenic silica was measured photometrically by a modified version of the method described by Mortlock and Froehlich (1989). The sample (12-14 mg) was treated with 1N HCl to remove carbonates and dried at 60°C. Organic matter was removed with a 5% H_2O_2 solution and the residue dried again at 60°C. Biogenic silica was dissolved by heating the sample at 85°C for five hours in Na_2CO_3 (7 %). After bringing the solution to room temperature, the silicate concentration was determined photometrically. Si-concentrations were muliplied by factor of 2.4 to calculate biogenic silicate contents (Mortlock and Froehlich, 1989). The standard deviation is ±1%.

Amino acids and hexosamines were analyzed after hydrolysis with 6 N HCl for 22 hours at 110°C. An aliquot of the hydrolysate (2ml) was transferred in a glass vial and evaporated to dryness. It was taken up in distilled water and evaporated twice to remove the remaining HCl. The residue was taken up in a citrate-buffer and an aliquot was injected into the Amino Acid Analyzer (LKB Pharmacia). Individual amino acids and amino sugars were separated by ion exchange chromatography and detected fluorometrically (Shimadzu FLD-6A) after derivatisation with an o-phthaldialdehyde/mercaptoethanol complex. Concentrations were calculated by comparison with a standard (0.1 mmol L^{-1}). The analytical error for individual amino acids and hexosamines varied between 5 and 10%. Only for methionine, histidine and ornithine the relative error was up to 25%. A correction factor of 1.4 was applied to hexosamines to compensate for loss during hydrolysis (Müller et al., 1986).

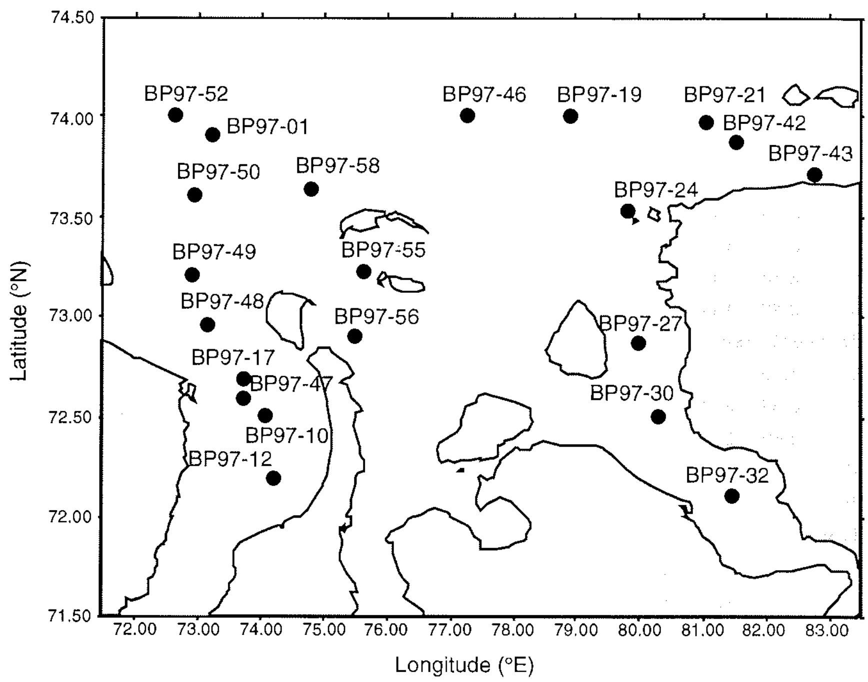

Fig. 1. Location of sampling stations in the Ob and the Yenisei estuaries (Kara Sea Expedition 1997).

Results

For presentation of the results the samples are grouped into four transects: Ob Estuary, Yenisei Estuary, East transect and Gydanskii Bay (Table 1).

Carbonate contents of the sediments are below 1% which is within the range of analytical error. Biogenic opal varies between 2.3 % and 4 % with an average of 2.9 %. Higher values are observed in the Yenisei Estuary (average 3.6%). Opal contents of >5% have been reported in Kara Sea surface sediments, especially in the inner bights of the Ob and Yenisei rivers and in the Kara Bay (Nürnberg, 1996). Generally, they decrease with increasing distance from the coast. Samples investigated in the present study are characterized by >90% lithogenic material. Organic carbon contents vary between 1 and 3% with an average of 1.6 %. Most of the higher values are observed in the Yenisei Estuary. Total nitrogen exhibits a uniform value of 0.2 %. The C/N ratios vary between 9 and 12 with an average of about 10.

Table 1: Organic matter in Kara Sea surface sediments (for abbreviations see text).

Station	Opal %	C_{org} %	N_{tot} %	C/N	AA [mg/g sed]	AA C%/Corg	AA N%/Ntot	AA Asp/ß-Ala	AA Glu/γ-Aba	AA Asp/Gly
1. Transect Ob Estuary										
12	2.42	1.86	0.2	10.29	3.34	7.7	25.7	9.8	9.1	0.8
10	2.98	2.21	0.2	10.22	4.93	9.7	30.9	16.8	15.9	1.0
47	3.09	1.46	0.2	9.8	3.66	11.0	35.3	8.7	11.1	0.7
17	2.25	1.54	0.2	9.43	3.94	11.0	34.4	12.8	12.5	0.8
48	2.37	1.55	0.2	9.35	3.09	8.6	25.7	9.7	12.1	0.6
49	2.90	1.54	0.2	9.21	4.25	12.0	35.2	11.0	12.7	0.7
50	2.55	1.46	0.2	8.93	2.70	8.0	23.9	11.0	13.1	0.7
01	2.72	1.65	0.2	11.25	4.62	12.0	43.9	12.1	10.8	0.8
52	2.42	1.86	0.2	10.29	3.97	12.4	37.7	11.0	14.6	0.7
2. Transect Yenisei Estuary										
32	3.59	2.79	0.2	12.13	7.12	11.2	44.7	11.6	19.0	0.7
30	3.94	2.23	0.2	12.36	4.82	9.4	38.7	10.5	15.4	0.7
27	3.63	2.12	0.2	10.76	3.05	6.1	21.4	12.0	13.6	0.9
24	3.67	1.44	0.2	9.51	3.68	10.9	34.5	13.2	12.8	0.8
19	3.1	1.98	0.2	8.91	5.26	11.4	34.0	12.9	13.4	0.8
3. Transect "East"										
52	2.44	1.38	0.2	8.91	3.97	12.4	37.7	11.0	14.6	0.7
01	2.72	1.65	0.2	11.25	4.62	12.0	43.9	12.1	10.8	0.8
46	4.02	2.17	0.2	9.08	6.49	13.1	39.3	13.3	15.6	0.8
19	3.1	1.98	0.2	8.91	5.26	11.4	34.0	12.9	13.4	0.8
21	2.86	1.72	0.2	9.72	4.24	10.6	33.3	12.3	11.6	0.8
42	2.68	1.00	0.1	9.71	2.32	9.9	35.1	8.8	8.8	0.6
43	3.65	1.83	0.2	9.08	4.80	11.2	35.9	10.2	12.9	0.7
4. Transect Gydanskii Bay										
56	2.42	1.19	0.1	10.37	2.80	10.1	36.1	8.9	11.7	0.6
55	3.07	1.75	0.2	9.73	3.94	9.7	31.2	9.4	11.1	0.6
58	2.6	1.02	0.1	9.4	2.53	10.7	32.6	9.7	11.8	0.7
Mackenzie River (Ittekkot, unpub.)										
		1.93	0.2	11.4		11.6	29.6			
		1.83	0.1	13.1						
		1.31	0.2	6.6						
		2.49	0.1	19.2						

Amino acid contents are in the range of 2.3 to 7.3 mg/g. They contribute 8 to 10% of the organic carbon and 20 and 45% of the total nitrogen. The amino acid spectra are dominated by the acidic amino acid, aspartic acid (Asp) and the neutral amino acids, glycine (Gly) and alanine (Ala). In general the neutral amino acids contribute between 4 and 16 mol%, followed by acidic (between 10 and 12 mol%), basic (1-5 mol%), aromatic (1- 3 mol%) and non-protein amino acids (1-2 mol%). In carbonate-free sediments, the ratio of aspartic acid to ß-alanine (Asp:ß-Ala) and glutamic acid to γ-aminobutyric acid (Glu:γ-Aba) are considered to be indicators of the degree of organic matter degradation (e.g. Degens, 1964). They vary between 9.7- 16.8 and 9.1-19; respectively. The lower values are observed within the Gydansky Bay. The ratios of aspartic acid to glycine (Asp:Gly), which are generally assumed to be indicators of the relative inputs from planktonic sources (calcareous versus siliceous plankton; Degens, 1970) are consistently < 1 consistent with the carbonate-free nature of the sediments.

Discussion

Comparison of the data with bottom water salinity, oxygen content and pH did not show any conclusive relationships between them and the nature of organic matter. These preliminary data show that the organic matter in surface sediments from the estuaries of the Ob and Yenisei as well as from the adjacent Kara Sea is probably derived from the similar source. Since lithogenic matter is the major sediment component, land-derived material could be a potential source of organic matter. In order to check this we compared our results with the available data on nitrogenous organic matter from soils from cool temperate regions (Sowden et al., 1977) and from suspended matter from rivers draining these regions such as for example the Mackenzie River which drains into the Beaufort Sea. Particulate organic carbon (POC) and particulate nitrogen (PN) contents measured in sediments are similar to POC and PN contents in suspended matter from the Mackenzie River (1.3 - 2.5 % and 0.13 - 0.21% respectively). Amino acid carbon and nitrogen contributed 11.6% of organic carbon and 30% of the PN (Ittekkot and Zhang, 1989).

The characteristics of nitrogenous organic matter, especially its amino fraction in soils, rivers and the sediments investigated by us are presented in Table 2. The cool temperate soils and the river suspended matter differ in the relative contributions of aspartic acid and glycine within the total amino acid fraction. Aspartic acid is lower and glycine higher than in sediments and river suspensions than in soils. This could result from the fractionation of soil organic matter into dissolved and particulate forms at the soil-river interface (Degens and Ittekkot, 1983). The nitrogenous organic matter in river suspensions and the sediments are remarkably similar.

Our preliminary conclusion is that the organic matter associated with surface sediments in the Kara Sea is derived from land. Organic matter derived from surface biological production is either rapidly recycled or is transferred to the offshore Arctic Basin. The nature of organic matter associated with the suspended matter collected during the study which is being examined at present will provide additional information on these processes.

Table 2: Distribution of nitrogen associated with individual amino acids in Kara Sea surface sediments. Nitrogen (N)mind Total amino acid-nitrogen (TAAN).

Amino Acids		N of TAAN	Ob	Rivers Yenisei	Mackenzie	Soil* cool temp.
		[%]	[%]	[%]	[%]	[%]
Acidic	aspartic acid (Asp)	9.7	9.1	10.0	8.7	12.1
	glutamic acid (Glu)	8.6	9.5	8.3	8.5	8.7
	total acidic	18.3	19,0	18.3	17.2	20.8
Basic	arginine (Arg)	14.0	13.0	14.0	12.9	10
	histidine (His)	3.5	3.4	3.2	4.1	4.2
	lysine (Lys)	9.0	9.0	8.6	6.1	7.6
	ornithine (Orn)	1.0	0.8	1.1	4.2	2.2
	total basic	27.5	26.0	26.9	27.2	24.0
Neutral	glycine (Gly)	13,0	13.0	13.0	13.3	11.4
	alanine (Ala)	9.1	9.1	9.4	9.8	8.4
	serine (Ser)	8.6	6.8	6.6	8.6	5.5
	valine (Val)	6.0	6.3	6.1	4.7	4.8
	threonine (Thr)	6.2	6.3	6.0	5.3	5.5
	leucine (Leu)	5.0	5.1	5.0	5.5	4.6
	iso-leucine (Ile)	3.3	3.5	3.4	3.1	2.9
	total neutral	51.2	50.0	49.5	50.3	43.1
Aromatic	tyrosine (Tyr)	0.5	0.6	0.6	0.8	1.1
	phenylalanine (Phe)	2.7	2.7	2.7	2.6	2.3
	total aromatic	3.2	3.3	3.3	3.4	3.4
Non-protein	ß-alanine (ß-Ala)	0.9	0.9	0.8	0.3	1.1
	γ-aminobutyric acid (γ-Aba)	0.7	0.7	0.6	0.1	1.0
	total non-protein	1.65	1.6	1.4	0.4	2.1

* from Sowden et al. (1977)

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QUANTITY AND QUALITY OF ORGANIC CARBON IN SURFACE SEDIMENTS OF THE OB AND YENISEI ESTUARIES AND ADJACENT COASTAL AREAS: MARINE PRODUCTIVITY VS. TERRIGENOUS INPUT

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Introduction

Two main mechanisms are controlling the accumulation of organic matter in the sediments of the Kara Sea. The large rivers Ob and Yenisei supply significant quantities of freshwater onto the shelf (Lisitsyn and Vinogradov, 1995; Bobrovitskaya et al., 1996; Johnson et al., 1997) and deliver terrigenous organic matter and aquatic algae. Additionally, marine organic matter is produced in the water column.

In order to distinguish between the different sources of the organic material maceral analysis, organic-geochemical bulk parameters and biomarkers (short- and long-chain n-alkanes, fatty acids and pigments) were used to determine the quality (marine vs. terrigenous) and quantity of the organic carbon fraction in the surface sediments taken during the 28th cruise of RV "Akademik Boris Petrov" (Matthiessen and Stepanets, 1998) (Fig. 1). Previous organic-geochemical investigations (i.e., total organic-carbon content (TOC), hydrogen indices (HI), C/N-ratios) indicate the importance of terrigenous input of organic matter (Galimov et al., 1996; Stein, 1996). Studies of lipid biomarkers in surface sediments in the Ob estuary show also a predominance of terrestrial constituents and an increase in planktonogenic and bacterial lipids further offshore (Belyaeva and Eglinton, 1997).

In complex systems such as the Eurasian continental margin characterized by high input of terrestrial/aquatic organic matter and strong seasonal variation in sea-ice cover and primary productivity, the interpretation of the organic geochemical data is much more complicated and restricted in comparison to similar data sets from low-latitude open-ocean environments (Fahl and Stein, 1998). Microscopical studies (maceral analysis/ palynology), however, allow a direct visual inspection of the particulate organic matter and allow to differentiate particles of different biological sources. Thus, a combination of both methods as shown in this study, yields a more precise identification of organic-carbon sources.

Methods

Analysis of Bulk Parameter and Biomarkers
Total nitrogen and organic-carbon contents were determined by means of a Heraeus CHN-analyzer (for details concerning the method see Stein, 1991). The hydrogen index (HI in mgHC/gTOC) was determined as described by Espitalié et al. (1977). The results are listed in Appendix 1.

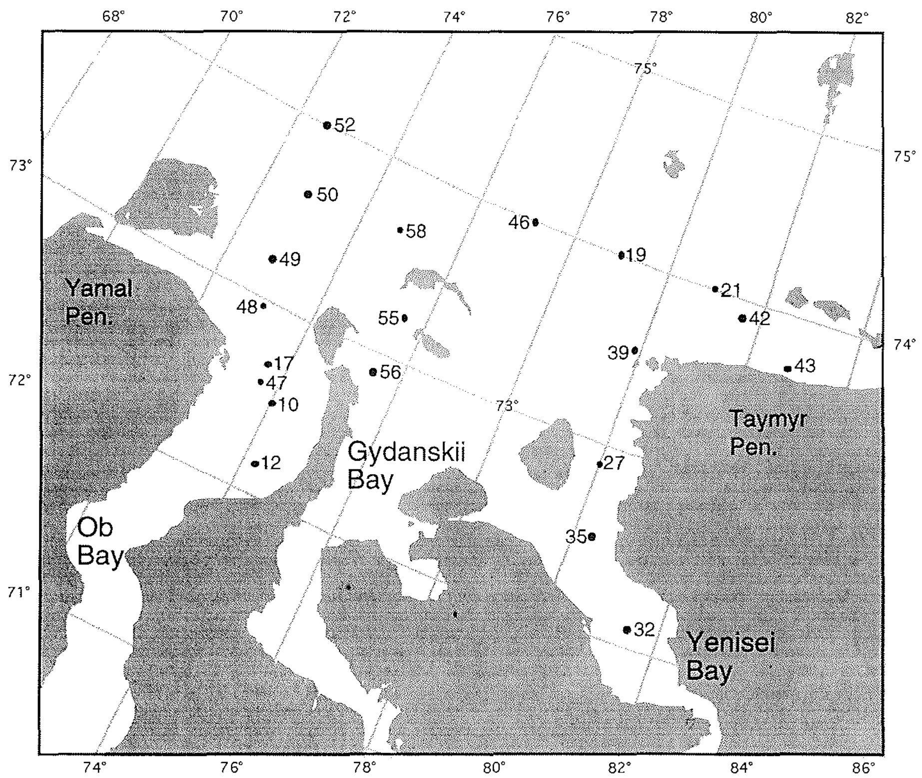

Fig. 1. Locations of stations.

For lipid analyses the surface sediment samples were stored at -80°C or in dichloromethane:methanol (2:1, by vol.) at -23 °C until further treatment. The sediment (2 g/parameter) was homogenised, extracted and purified as recommended by Folch et al. (1957) and Bligh and Dyer (1959). An aliquot of the total extract was used for analyzing n-alkanes and fatty acids.

n-Alkanes

The alkanes were separated from the other fractions by column chromatography with hexane. The composition was analysed with a Hewlett Packard gaschromatograph (HP 5890, column 50 m x 0.25 mm; film thickness 0.25 µm; liquid phase: HP 1) using a temperature program as follows: 60 °C (1 min), 150 °C (rate: 10 °C/min), 300 °C (rate: 4 °C/min), 300 °C (45 min isothermal). The injection volume is 1 µl (Cold Injection System: 60 °C (5 s), 300 °C (60 s, rate: 10 °C/s). Helium was used as carrier gas. The composition was qualified by a standard mixture; for the quantification squalane was added before any analytical step.

Fatty acids

An aliquot of the total extract was used for preparing fatty acid methyl esters and free alcohols by transesterification with 3 % concentrated sulfuric acid in methanol for 4 hours at 80 °C. After extraction with hexane the composition was analysed with a Hewlett Packard gaschromatograph (HP 5890, column

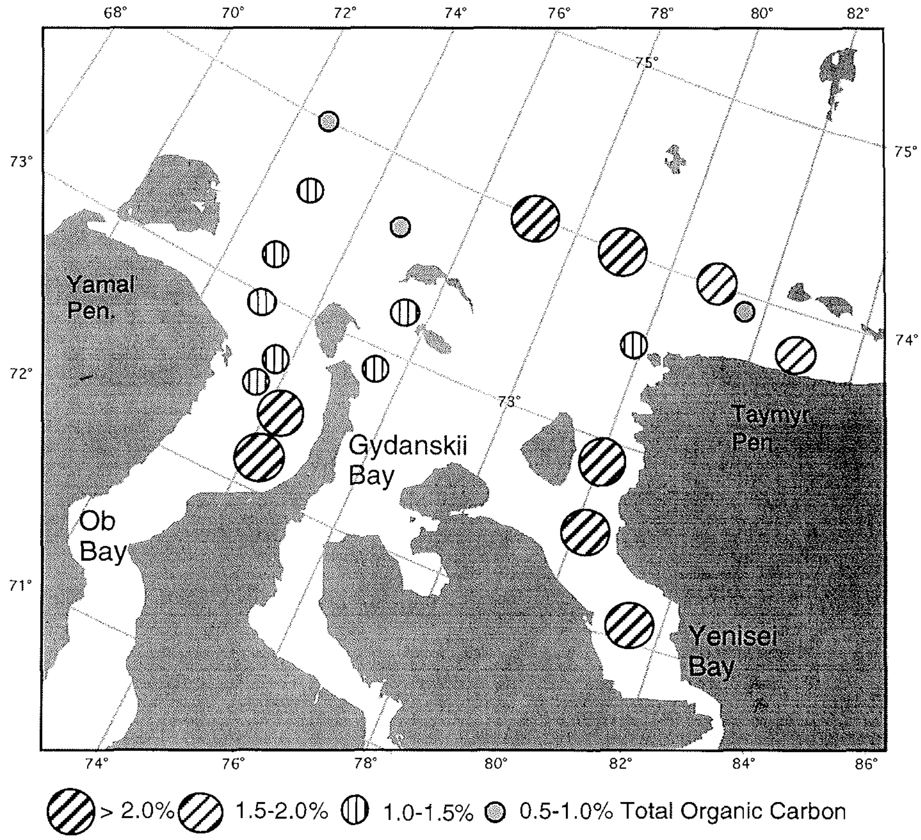

Fig. 2. Distribution of total organic carbon in surface sediments.

30 m x 0.25 mm; film thickness 0.25 µm; liquid phase: DB-FFAP) using a temperature program as follows: 160 °C, 240 °C (rate: 4 °C/min), 240 °C (15 min isothermal) (modified according to Kattner and Fricke, 1986). The injection volume is 1 µl. The fatty acids and alcohols were identified by a standard mixture (Marinol standard was kindly made avaibable by J.R. Sargent, Scotland). For quantification an internal standard (19:0 fatty acid methyl ester) was added.

Pigments

The tetrapyrrolic pigments were determined by measuring the absorbance of their solvent extract (90% acetone) at a wavelength of 410 nm (Rosell-Melé, 1994; Rosell-Melé and Koç, 1997). Additionally the measurement was carried out at 645 and 663 nm to determine chlorophyll abundances. The turbidity factor (absorbance at 750 nm) was substracted.

Maceral Analysis

The source of particulate organic matter can be characterised by determination of the different maceral groups. The classic maceral concept is based on coal petrography studies. In general, macerals are divided into the three main groups vitrinite/huminite, inertinite and liptinite, and several subgroups,

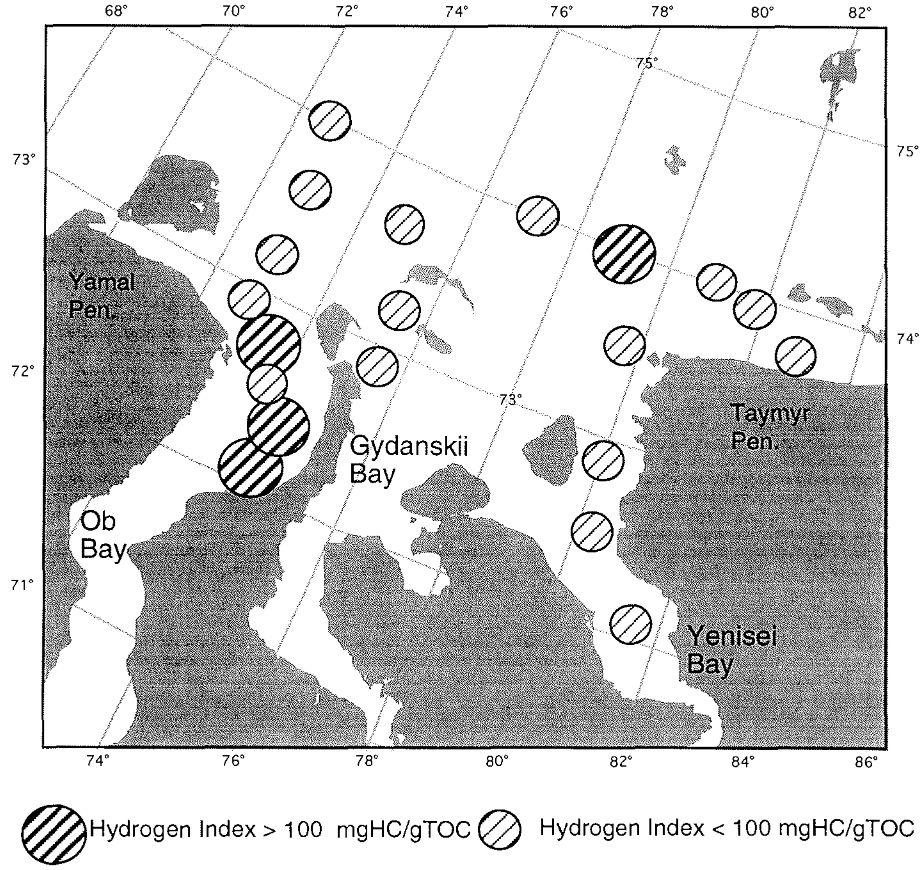

Fig. 3. Hydrogen index in surface sediments.

according to the nomenclature described by Stach et al. (1982). For our investigations of marine sediments of high-latitudes a modification of the classic maceral concept was necessary. We distinguish between terrigenous and marine macerals. Terrigenous macerals include the main groups vitrinite/ huminite, inertinite and liptinite and different subgroups (e.g., textinite, sporinite, cutinite etc.). Fragments (<10μ) of vitrinite/huminite and inertinite are classified as detritus and, in case of particles showing fluorescence, as liptodetrinite. Liptodetrinite can be originated from marine as well as from terrigenous macerals and must be considered as an own group. Chlorophycean algae such as *Botryococcus* or *Pediastrum* are classified as limnic-brackish alginite and belong to the terrigenous macerals. Marine macerals include finely lamellar alginite (lamalginite) (e.g., Senftle et al.,1993; Hutton et al., 1980) and dinoflagellate cysts. Fragments of dinocysts and lamalginite with a grain size >10μ are considered as an own group and are classified as "marine liptinites".

Maceral analysis was performed on bulk sediments embedded in a cold-setting epoxy-resin which was subsequently grounded and polished.

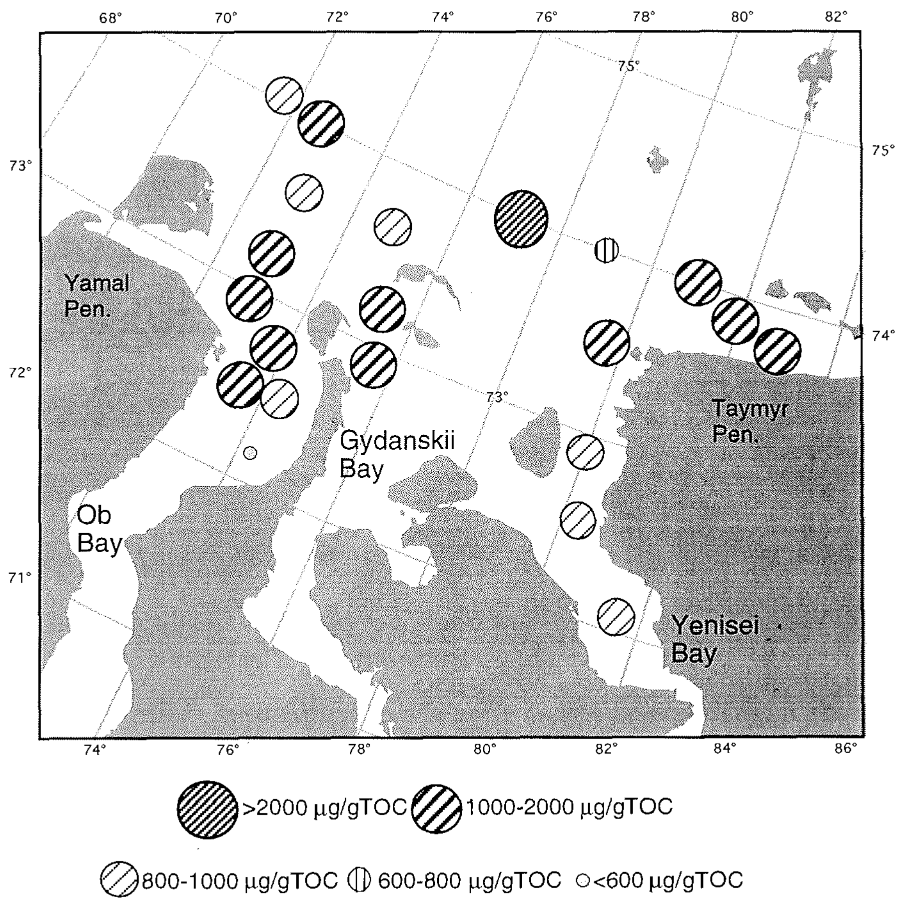

Fig. 4. Distribution of short-chain fatty acids in surface sediments.

The amount of the different maceral groups were obtained by counting at 1000x magnification using incident light and blue-light exication. At least 200-300 macerals were counted as grain % under consideration of their grain size. In the subsequent evaluation the different sizes were converted to the grain size of 10-20µ in diameter. Sampling of the surface sediments is described in Matthiessen et al. (1998).

Results and discussion

Microscopical and organic-geochemical analysis revealed that the composition of organic matter in surface sediments from the western part of the investigation area (Ob Bay, Gydanskii Bay) differ from the eastern part (Yenisei Bay). Total organic carbon (TOC) maxima of >2% occur in both river mouths (Fig. 2). The high TOC contents in the Ob Bay, however, correlate well with hydrogen index (HI) values > 100 mgHC/gTOC (Fig. 3) indicating a significant influence of marine organic matter whereas the high TOC contents in the Yenisei Bay commonly correspond to low HI values (< 100 mgHC/gC)

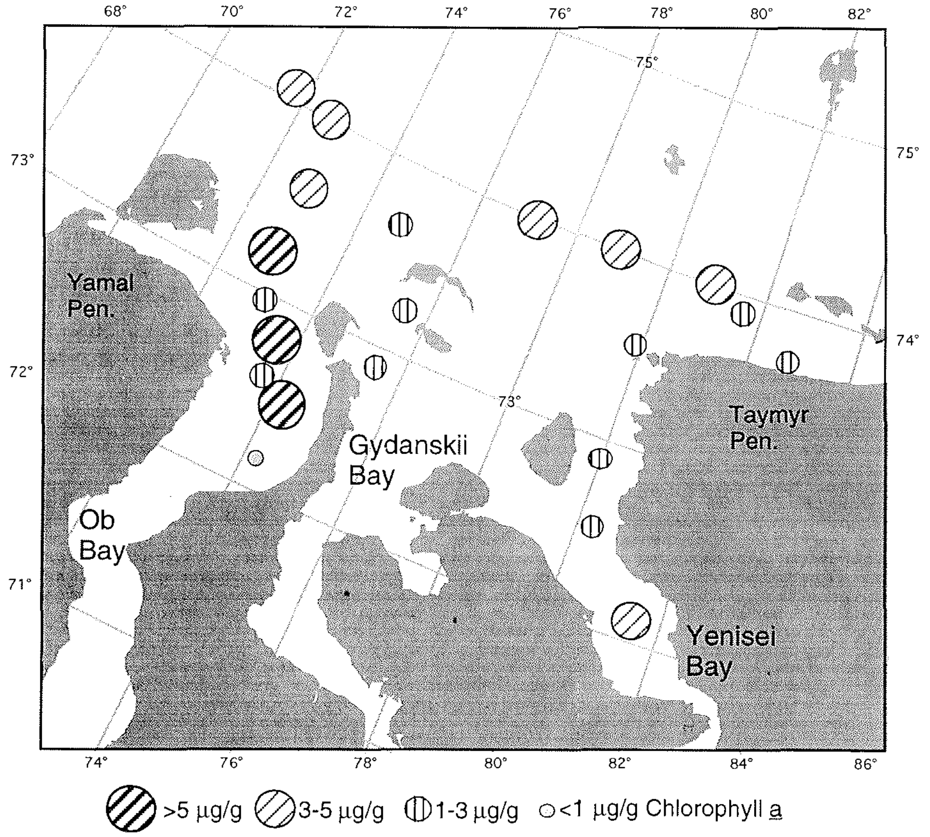

Fig. 5. Distribution of chlorophyll a in surface sediments.

indicating the predominance of terrigenous organic carbon. This is also supported by the biomarker results (Figs. 4, 5). High amounts of long-chain n-alkanes indicate dominently terrigenous organic matter (Fig. 6). Only in the western part (and north of Taymyr Peninsula) the highest amounts of short-chain fatty acids (Fig. 4) and chlorophyll a (Fig. 5) suggest increased marine organic matter being preserved in the surface sediments. The high accumulation of inorganic as well as organic (mostly terrestrial, but partly also marine) material in the river and seawater mixing zone of the river mouths is probably due to "mariginal filter effect". This effect was described by Lisitsyn (1995) suggesting that 93-95% of the suspended matter was accumulated in this zone.

In general, the microscopical investigations support the bulk parameters and the biomarker data and show that the POM of the Kara Sea sediments is dominated by terrigenous macerals (ø73%; Fig. 7). The results show relatively high amounts of marine organic matter occuring in the western part of the investigation area (up to 35%), in the Ob Bay (up to 36%) and Gydanskii Bay (up to 27%). In the eastern part and Yenisei Bay the abundance of marine macerals is insignificant (< 8%), and the sediments are mainly dominated by terrigenous macerals.

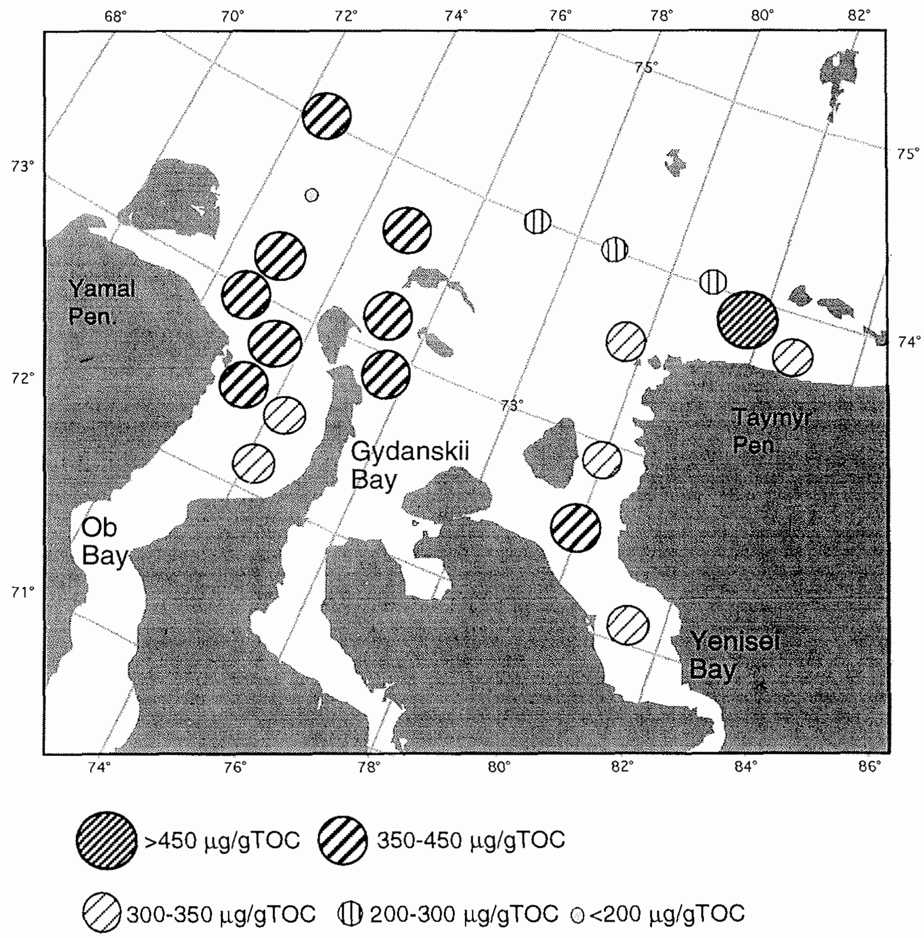

Fig. 6. Distribution of n-alkanes in surface sediments.

Limnic-brackish alginite *Pediastrum* and *Botryococcus,* partially good preserved, occur in the Ob and Gydanskii bays (up to 7%) and in small amounts further north in samples of the 74°-Profile. These algae groups are usually adapted to freshwater conditions and indicate river inflow (e.g. Kunz-Pirrung, in press.). In contrast only small amounts of these algae occur in the Yenisei Bay.

Relatively well preserved terrigenous macerals, e.g. textinite, a subgroup of huminite, was observed in the south of the river mouths. In comparison the area further offshore (74°-Profile) is characterised by an increase of terrigenous detritus of huminte/ vitrinite (grain sizes <10µ) because of a stronger fragmentation due to a further lateral transport (Fig.8 A,B).

Fast environmental changes, e.g. strong seasonality of salinity of the surface water layer (Churun and Ivanov, 1998), sea-ice cover and river inflow in the

Kara Sea, make comparisions of data derived from organic matter in the surface water layer with data from organic matter preserved in surface sediments difficult.

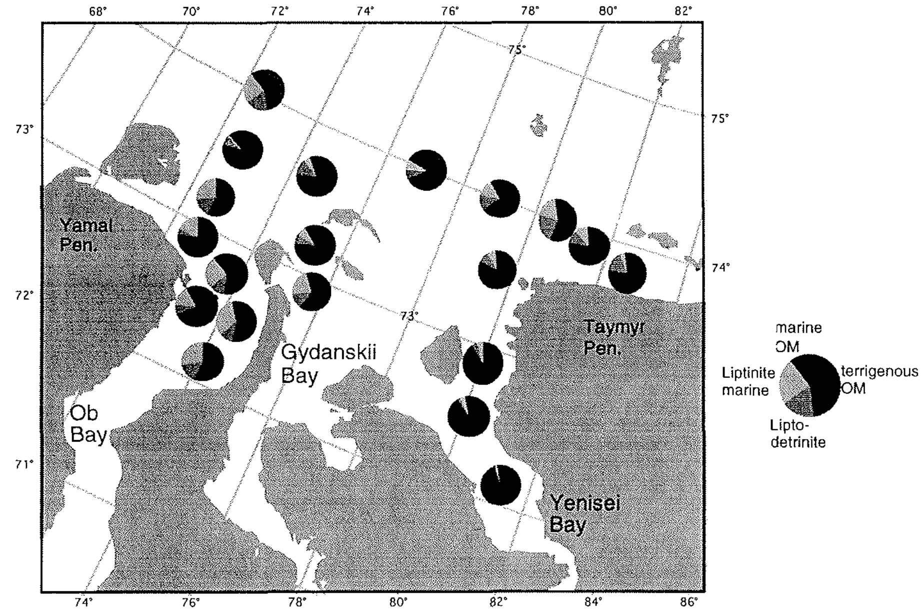

Fig. 7. Distribution of maceral groups in surface sediments.

For example the nutrients in the surface water of the eastern part are already depleted (0-0.5 µM nitrate) and due to this the chlorophyll a concentration is rather high (Nöthig et al., this volume). This "produvtivity" signal is not reflected in the surface sediments. In the western part it is just the opposite. Due to the distribution of biomarkers and macerals indicating increased marine organic matter preserved in the surface sediments, we would expect high concentrations of chlorophyll a and as well as in the eastern part depleted nutrients. The nitrate concentration, however, is still (or already) high, and the pigment contents are rather low.

The distribution of palynomorphs in the surface water layer also shows discrepancies in the composition of organic matter of the suspension load and in the surface sediments (Matthiessen and Boucsein, this volume).

For that reason further studies considering the seasonal variability are needed (e.g., sediment traps).

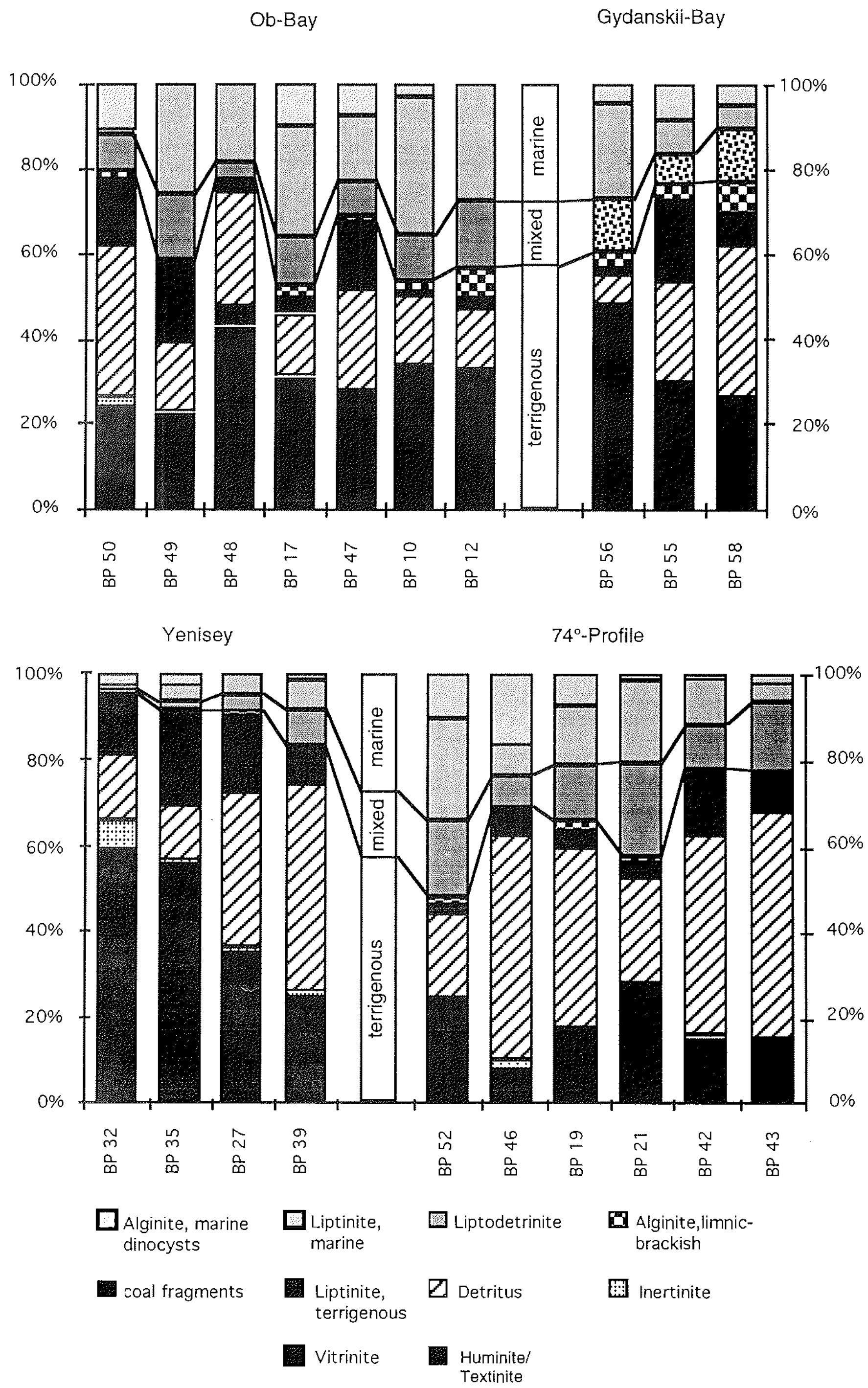

Fig. 8. Distribution of maceral groups along the transects.

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Appendix 1: Organic geochemical parameter of surface sediments.

Station (MUC)	N_{tot} (%)	N'_{tot}	C/N	$CaCO_3$ (%)	TOC (%)	HI mg CO_2/ g TOC	OI mg CO_2/ g TOC	T_{max} (°C)
BP97-01	0.236	0.194	5.65	2.2	1.33	59	309	386
BP97-10	0.235	0.251	8.65	0	2.04	148	319	461
BP97-12	0.279	0.289	7.98	0	2.23	146	314	480
BP97-17	0.176	0.176	7.67	0.7	1.35	163	319	479
BP97-19	0.275	0.303	7.55	0	2.08	123	241	390
BP97-21	0.216	0.238	7.88	0	1.70	62	229	382
BP97-27	0.231	0.273	9.95	0	2.30	62	269	398
BP97-32	0.270	0.318	11.77	0	3.18	71	202	417
BP97-35	0.208	0.229	10.99	0	2.29	63	238	405
BP97-39	0.169	0.158	6.9	1.4	1.16	76	290	392
BP97-42	0.097	0.091	7.33	1.0	0.71	62	271	388
BP97-43	0.239	0.264	8.19	0	1.96	63	311	383
BP97-46	0.263	0.294	7.83	0	2.06	83	243	397
BP97-47	0.159	0.161	7.94	2.8	1.27	74	338	401
BP97-48	0.142	0.143	7.66	0.9	1.09	71	331	398
BP97-49	0.172	0.176	7.42	1.4	1.28	72	349	389
BP97-50	0.203	0.204	7.05	0.7	1.43	82	272	393
BP97-52	0.130	0.122	6.72	1.1	0.87	92	265	395
BP97-55	0.197	0.184	7.09	2.6	1.40	66	372	392
BP97-56	0.146	0.134	6.92	3.2	1.01	65	357	393
BP97-58	0.120	0.09	5.62	2.6	0.68	70	366	338

MANGANESE, IRON, AND NUTRIENTS IN PORE WATER PROFILES FROM THE OB AND YENISEI ESTUARIES (KARA SEA)

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Introduction

Coastal marine environments are of special interest in order to estimate the influence of river runoff on geochemical budgets and composition of the oceans. Thus, rivers discharging into the extensive shelf seas around the Arctic Ocean must be assumed to supply large amounts of nutrients and trace metals but there is a general lack of quantitative estimates of fluxes and their seasonal variability. Therefore, an iron limitation is probably to be expected in the Arctic Ocean in contrast to the Antarctic frontal zone (Martin and Gordon, 1988) because of the extensive arctic shelf areas where iron might be deposited. In the Kara Sea the behaviour of nutrients and metals is influenced especially by seasonal changes in river discharge and variations in rates of sediment resuspension. Furthermore, the seasonally variable benthic activity is coupled with the decomposition of organic resulting possibly in periods of anoxic conditions, and thus contribute to the behaviour and pathways of metals and nutrients in the shallow estuaries. However, there are no estimations whether the internal cycling or the export flux from the estuaries is dominating.

During the expedition to the inner Kara Sea in September 1997 pore water samples were taken in order to study gradients of manganese and iron concentrations and the redox conditions in sediments during a summer situation. Preliminary results obtained on sediments from the mixing zone as well as from the riverine and marine stations of the transects in the rivers Ob and Yenisei are presented.

Methods

Surface sediments were obtained by a multi corer (MUC) and giant box corer (GKG) at 11 stations (Fig. 1). Pore water sampling and squeezing was carried out by Dr. V. Samarkin and the group of Dr. L. Kodina during the cruise while the chemical analysis was carried out at the Alfred Wegener Institute.

Nitrate, silicate and phosphate were analyzed by means of a Technicon I Auto-analyzer according to the method of Grasshoff et al. (1983). Precision has been better than 1,5% for nitrate, 2,1% for phosphate and 1,7% for silicate. Manganese and iron were measured by means of flameless atom absorption spectroscopy calibrated with aqueous standard. Besides, iron was measured with an additional standard. The standard deviation has been lower than 5%.

All data are listed in Table 1. Silicate and phosphate concentration profiles will not be discussed because interpretations based on the few data may be misleading.

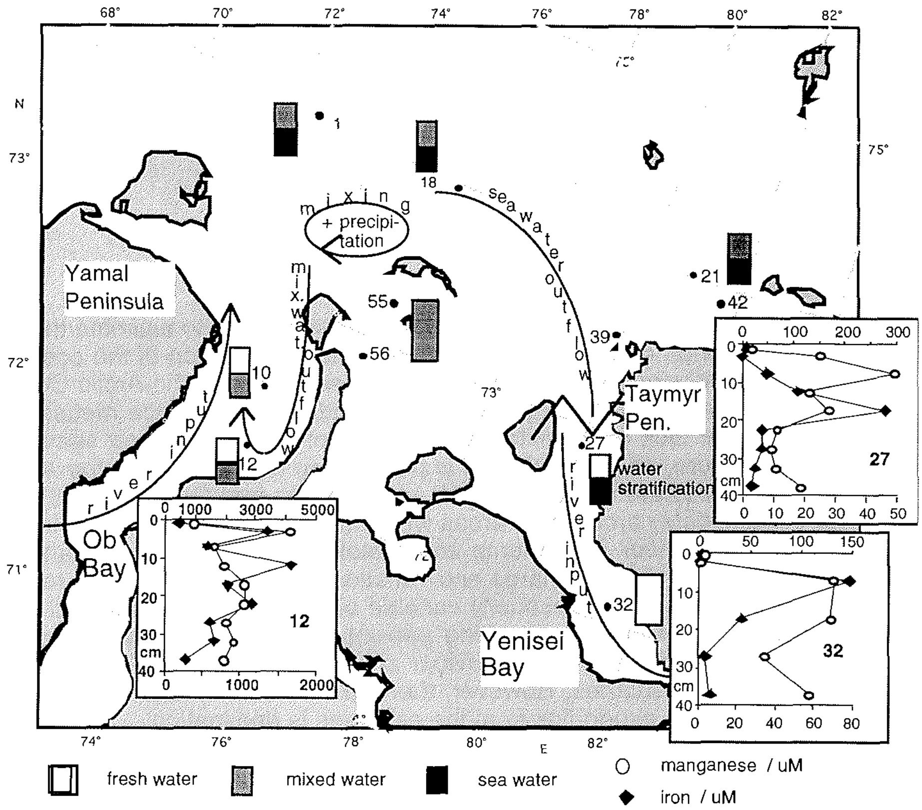

Fig. 1. Sample locations and selected pore water profiles.

Results and discussion

Nitrate

The nitrate pore water profiles show an inhomogeneous pattern (Table 1). The profiles from the Ob Estuary are characterized by very low concentrations and gradients. Nitrification does not take place or only to a small extent. The profiles from the Yenisei Estuary at stations 55, 39 and 21 display a nitrification as well as a denitrification zone. That is the more typical shape of pore water profiles which reflect degradation of organic matter by oxygen in the nitrification zone. According to the degradation sequence, denitrification is caused by reduction of nitrate if oxygen is depleted. However a whole denitrification was not reached in the measured profiles. At stations 56, 32, 27 and 42 a nitrification peak exists close to the sediment surface, and the deeper parts of the profiles are still irregular. These type of profiles can not be assigned to a specific region in the investigation area.

Manganese and iron

The pore water profiles from the outer estuaries are comparable with profiles from sediments underlying the freshwater plume of the Lena River in the eastern Laptev Sea (unpubl. data). The concentration gradients of the metal profiles are clearly different between Ob and Yenisey estuaries. The highest con-

Table 1. Nutrients, manganese and iron in pore water profiles (n.D.: no data).

Station	Core Depth (cm)	NO3 (μM)	NO2 (μM)	Si (μM)	PO4 (μM)	Mn (μM)	Fe (μM)
55	0-2	7.33	0.68	160.40	0.03	4.84	0.02
	2-5	13.14	0.62	266.56	2.62	150.71	2.88
	5-10	15.12	0.77	234.68	2.40	97.01	6.45
	10-15	17.84	0.93	198.20	1.62	99.20	3.62
	20-25	16.96	0.98	384.00	2.83	184.93	3.60
	30-35	17.18	0.91	372.00	1.30	95.01	2.67
	40-45	9.50	1.40	380.00	1.80	190.64	1.67
56	0-2	13.40	1.74	142.59	0.06	20.40	0.39
	2-5	4.95	0.53	382.56	0.45	n.D.	n.D.
	5-10	7.53	1.40	254.70	0.09	412.27	0.39
	10-15	4.34	0.83	269.90	2.12	167.09	1.40
	20-25	7.90	2.20	255.60	0.30	101.27	0.38
	30-35	16.80	0.91	342.40	1.07	271.20	0.90
39	2-5	4.95	0.60	202.00	2.56	145.61	0.26
	5-10	5.74	1.20	196.40	2.30	105.21	3.58
	10-15	14.50	1.75	164.65	3.04	97.56	4.70
	15-20	9.27	1.29	152.00	4.32	33.49	3.29
	20-25	8.15	1.70	150.00	3.04	100.66	5.10
18	0-1	18.29	2.08	61.80	1.05	53.04	0.20
	1-3.5	11.99	1.51	148.88	1.43	55.01	0.20
	3.5-7.5	9.82	0.76	135.31	0.73	43.96	n.D.
	7.5-21.3	7.60	0.78	127.73	4.80	29.81	nD.
1	0-2	2.73	0.38	190.45	3.30	112.85	0.02
	2-5	5.24	0.64	166.63	1.36	241.54	2.78
	5-10	5.48	0.64	155.00	4.89	217.51	9.13
	10-15	11.05	1.46	173.40	7.84	154.71	17.73
27	0-2	4.51	0.38	43.96	3.01	19.51	1.42
	2-5	3.78	0.32	62.00	2.52	151.80	0.27
	5-10	16.60	0.60	22.20	2.26	293.59	7.95
	10-15	2.60	1.00	85.27	6.40	130.69	17.91
	15-20	3.10	0.78	81.75	10.80	166.91	46.55
	20-25	10.30	1.05	96.12	7.80	67.71	6.62
	25-30	2.15	0.65	100.75	9.60	53.88	5.91
	30-35	1.98	0.76	135.79	7.80	63.71	3.93
	35-40	1.68	0.70	120.41	13.20	111.21	3.24
32	0-1	8.30	0.75	64.10	0.33	5.82	1.47
	1-3	16.35	0.94	42.60	0.20	4.19	0.09
	5-10	2.30	0.30	152.80	0.57	132.33	78.20
	15-20	2.67	0.38	210.00	0.30	128.14	23.00
	25-30	3.67	0.64	388.80	0.62	62.80	3.09
	35-40	4.52	0.61	367.20	0.35	108.12	5.73
10	0-2	3.65	0.43	96.80	3.15	569.71	0.03
	2-7	5.35	0.63	104.22	3.01	313.07	0.05
	13-21	6.52	0.76	254.37	0.70	303.97	2.06
	24-35	6.40	0.99	162.95	0.14	345.83	1.15
21	0-2	2.47	0.53	132.00	3.00	190.03	0.04
	2-5	5.95	1.03	136.90	2.88	418.64	1.50
	5-10	8.68	1.11	131.40	2.68	317.62	17.78
	10-20	6.52	0.83	154.40	5.04	184.75	3.29
	20-30	6.95	0.82	181.86	10.72	144.52	10.78
	30-40	1.64	0.86	194.60	17.40	5.46	3.06
42	0-2	3.66	0.30	152.90	1.20	23.97	0.11
	2-5	4.53	0.75	170.70	4.20	212.96	0.16
	5-10	11.52	1.34	141.29	3.62	97.20	2.54
	10-15	3.86	1.49	152.60	5.28	102.84	3.53
	20-25	7.73	1.49	195.85	8.60	111.94	4.48
	30-35	11.60	1.85	144.36	7.60	67.11	1.85
	40-45	6.50	2.30	126.38	n.D.	59.83	0.47

Table 1: cont´d

Station	Core Depth (cm)	NO3 (µM)	NO2 (µM)	Si (µM)	PO4 (µM)	Mn (µM)	Fe (µM)
12	0-2	5.23	0.99	176.73	0.53	946.49	182.99
	2-5	5.90	1.17	152.07	0.75	4084.46	1342.17
	5-10	3.91	1.35	116.80	0.24	1599.93	551.48
	10-15	3.27	0.78	83.85	0.51	1933.02	1650.49
	15-20	3.77	0.85	82.40	0.05	2615.58	808.95
	20-25	5.28	1.22	72.91	0.01	2593.74	1139.12
	25-30	3.98	0.95	65.76	0.01	2004.00	603.76
	30-35	2.40	0.99	65.87	0.07	2273.39	63.21
	35-40	5.13	1.09	102.91	0.01	1974.88	284.69

centrations were measured in the inner Ob Estuary (stations 12, 10). Furthermore, an upward diffusion of Mn^{2+} can be expected. The base of the oxidized layer is much closer to the sediment-water interface in these profiles. Some of the upward diffusing Mn^{2+} can escape from this thin oxidized layer and enter into the water column. By this way resuspended manganese would contribute to the budget of the river run-off. In comparison the pore water profiles in the inner estuary of the Yenisey indicate that the reducing zone is located deeper in sediments. Additionally reduced metals are mobilized only slightly and diffusion of Mn^{2+} into the overlying water column does not occur.

The different pore water profiles of Ob and Yenisey estuaries seem to be the result of different water circulation and mixing (Fig. 1, cf. Churun and Ivanov, 1998). The bottom and surface waters mixed at the head of the Ob Estuary. Hence the deep water, which is flowing into the estuary, is a mixture of marine saline deep water and riverine freshwater and its dissolved load. Thus, sediment profiles will be influenced by precipitation processes within the estuarine mixing zone. However, no stations with mixed water were sampled in the Yenisei Estuary. There, a water stratification is produced by freshwater outflow at the surface and saline bottom water inflow. This water stratification seems to prevent a precipitation of dissolved riverine matter in the inner estuary which is transported further offshore and eventually precipitates in the inner Kara Sea or even in the adjacent Arctic Ocean or Laptev Sea.

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RADIO - GEOCHEMISTRY

DISTRIBUTION OF ANTHROPOGENIC RADIONUCLIDES IN THE ESTUARIES OF OB AND YENISEI RIVERS AND ADJACENT KARA SEA

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The present radioecological state of sea water of the Arctic basin which is exposed to considerable radioactive contamination has generated a great deal of public and scientific interest, since the ocean water is characterized by great mobility and transports this contamination through a variety of migration pathways over long distances. Radionuclides in marine water may have many sources, including natural ones such as cosmic radiation and rocks, atmospheric and oceanic transport from sites of accidents, weapon tests and nuclear waste disposal in the ocean and on land. It is well known that unauthorized wastes from nuclear sources have entered the sea. The behaviour of radionuclides in the marine environment depends both on their chemical nature and the physicochemical situation in the basin. The investigation of distribution and migration pathways of artificial radionuclides as tracers of geochemical processes is one of the important problems of sea water geochemistry.

One of the sources of anthropogenic pollution in the Kara Sea are the catchment areas of the large Siberian rivers Yenisei and Ob, where radioactive wastes from reprocessing plants can be discharged. Roskomgidromet estimated that from 1961 to 1989 the supply of radionuclides by the rivers Ob and Yenisei contributed 110 TBq Cs-137 and 1100 TBq Sr-90 to the Kara Sea (Yablokov et al., 1993).

The radioactive elements are transported with river water to the Kara Sea passing through a zone of interaction between the river and sea, where the distribution and behaviour of elements can undergo significant changes. At the contact of fresh river and salty sea waters environmental conditions such as current speed, salinity, pH, chemical structure sharply vary resulting in deposition of up to 20-40 % of dissolved substances and up to 90-95 % of particulate matter in this zone (Lisitzyn, 1995). The smallest particles and colloids of particles are carriers of hydrolytic radionuclides (Pu-239,240). In internal crystal structures of clay minerals significant amounts of Cesium radionuclides can be accumulated (replacing ions such as potassium in interjunction - type intervals of minerals). These processes are less effective for the radionuclide Sr-90, which is rather stable in watery fluids and the accumulation in crystal structures is less characteristic (Kusnetsov et al., 1994).

It is obvious that the investigation of distribution of artificial radionuclides in the estuaries of the rivers Ob and Yenisei and adjacent Kara Sea is of special interest from the radioecological point of view of the investigation area as a natural geochemical barrier which can be an effective filter for the dispersal of chemical elements and their radioactive isotopes.

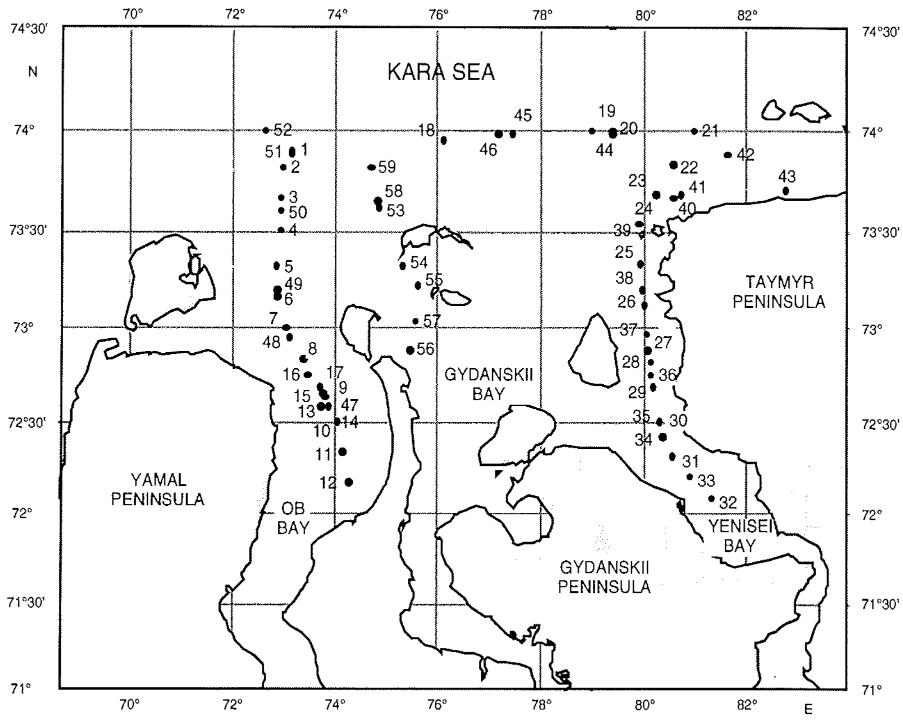


Fig. 1. Sample stations during the 28th cruise of RV "Akademik Boris Petrov" in 1997 (52 = BP97-52).

The distribution and behaviour of radionuclides in water is determined by the location of their sources and geochemical factors such as composition of particulate matter in water, reworking of organic substances and resulting redox conditions in the sediments and hydrophysical parameters of sea water.

Based on data from experiments which have been carried out by us in 1995, the distribution of radioactivity in sediment and water of the Arctic shelf seas, first of all of the Kara Sea, is rather patchy, and the highest concentrations of the radionuclides Cs-137 and Pu-239,240 were found in the southeastern part of the sea (Galimov et al., 1996). These investigations were continued on a larger scale during the 28th cruise of RV "Akademik Boris Petrov" in 1997 (Matthiessen and Stepanets, 1998) within the framework of an cooperation agreement between the Vernadsky Institute of Geochemistry and Analytical Chemistry and the Alfred Wegener Institute for Polar and Marine Research to study the nature of continental run-off from the Siberian rivers and its behaviour in the adjacent Arctic basin.

The experimental investigations were carried out in the estuaries of the rivers Ob and Yenisei, and the southern part of the Kara Sea where 59 stations were sampled (Fig. 1).

The main tasks of radiogeochemical research were to study the horizontal and vertical distribution of the isotopes cesium, strontium and plutonium in water and sediments, and to estimate the influence of natural environmental parameters on laws governing the distribution and migration of radionuclides in the investigation area. For interpretation of the results, hydrophysical parameters of the water column (Churun and Ivanov, 1998), and the description of sediment cores were used (Matthiessen et al., 1998).

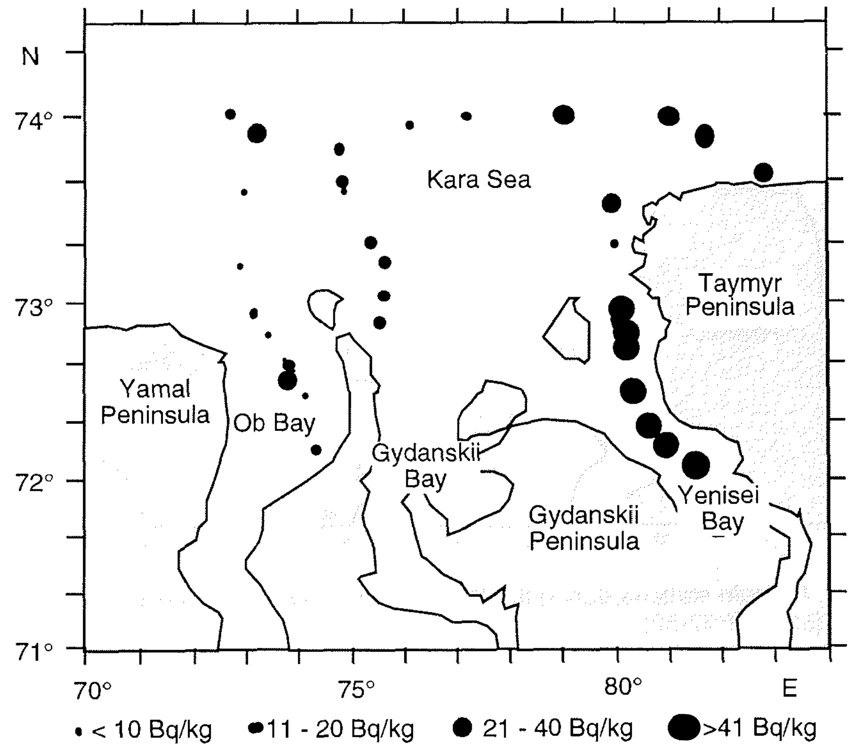


Fig. 2. Distribution of Cs-137 in bottom sediments (0-2cm).

Sampling and Analytical Methods

Sediments were sampled with a box corer (50x50x60cm) and an "Okean"-grab, with subsequent subsampling with a plastic tube having an inner diameter of 10 cm. The cores were cut in 1-2 cm slices, and samples were dried at a temperature of 60-80°C.

Water was sampled with a large volume sampler (200 l Batomat) or taken by a pump through a plastic pipe system, and filled in storage tanks of 150 l volume. Before analysis some samples were filtered through a cartridge filter to remove suspended matter > 0.45 μm.

The greatest amount of data was obtained for Cs-137 contents, and to a smaller extent for Sr-90 and Pu-239,240. Cs-137, Sr-90, and Pu-239,240 in water samples, and Sr-90 and Pu-239,240 in sediment samples were determined with a radiochemical method, for the analysis of Cs-137 in sediments we used direct α-measurements without decomposition of the sample.

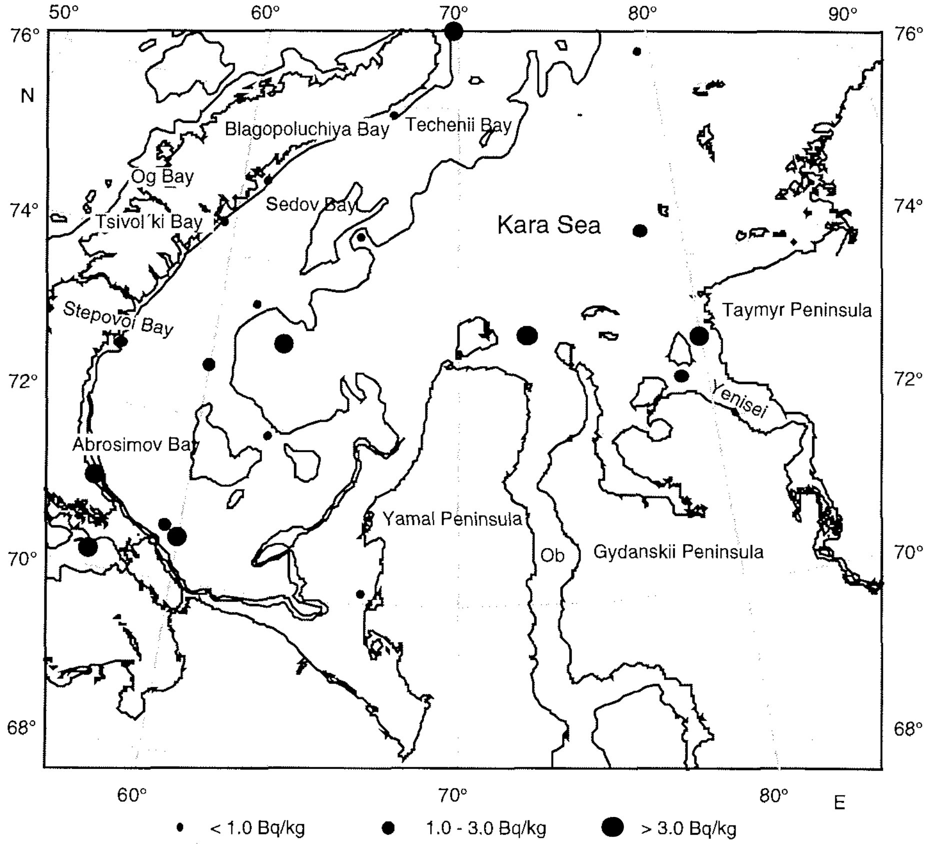


Fig. 3. Distribution of Pu-239,240 in bottom sediments (0-2cm).

Measurement of the radioactivity of Cs-137 in sediment samples was carried out in a low-background installation with semiconductor Ge(Li) (DGDK-80) detectors.

Cs-137 was determined in water samples of 100 l volume using the sorption method under dynamic conditions with subsequent γ-spectrometer measurements on concentrates. Co-ferrocianid, fixed on an organic matrix, was used as quality sorbent for concentrating cesium (Stepanets et al., 1992).

The determination of Sr-90 in water samples included precipitation of strontium carbonate with subsequent radiochemical cleaning and final precipitation of strontium as oxalate using a combination of analytical methods. Sr was measured in a low-background installation with flowing gas counting the energy of Sr-90 or Y-90 (Kremlyakova, 1993). Analysing sediments, acids were used to dissolve the samples and then analysed according to the above described procedure.

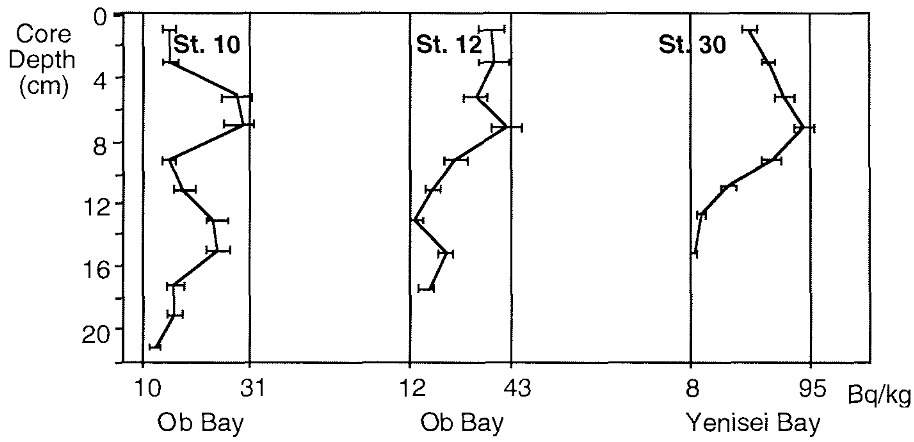


Fig. 4. Concentration of Cs-137 vs. depth in 1997.

The analysis of plutonium in water samples consisted of precipitation of Pu with iron hydroxide (from a volume of 100 l), subsequent radiochemical cleaning and adsorbtion of Pu on LaF_3. Precipitates were separated on a membrane filter and activity measured on α-spectrometer. For extration of Pu from sediments samples were boiled in 7M HNO_3 with $KBrO_3$, and then were further processed as water samples for Pu analysis (Pavlotskaya et al., 1984).

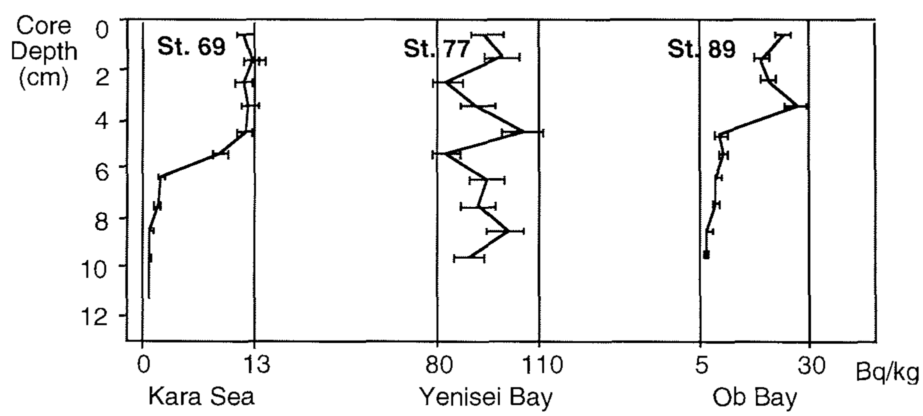
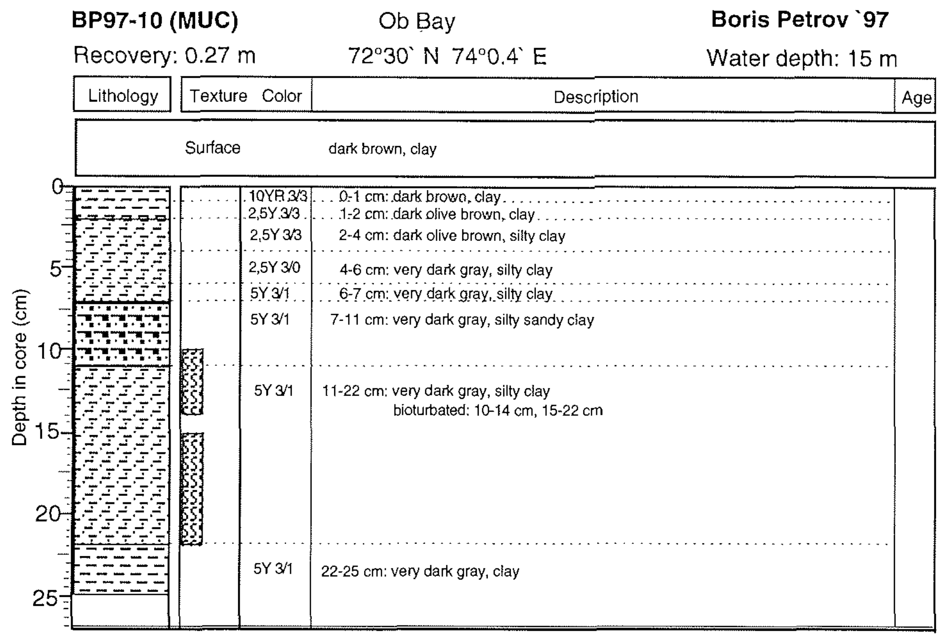


Fig. 5. Concentration of Cs-137 vs. depth in 1995.



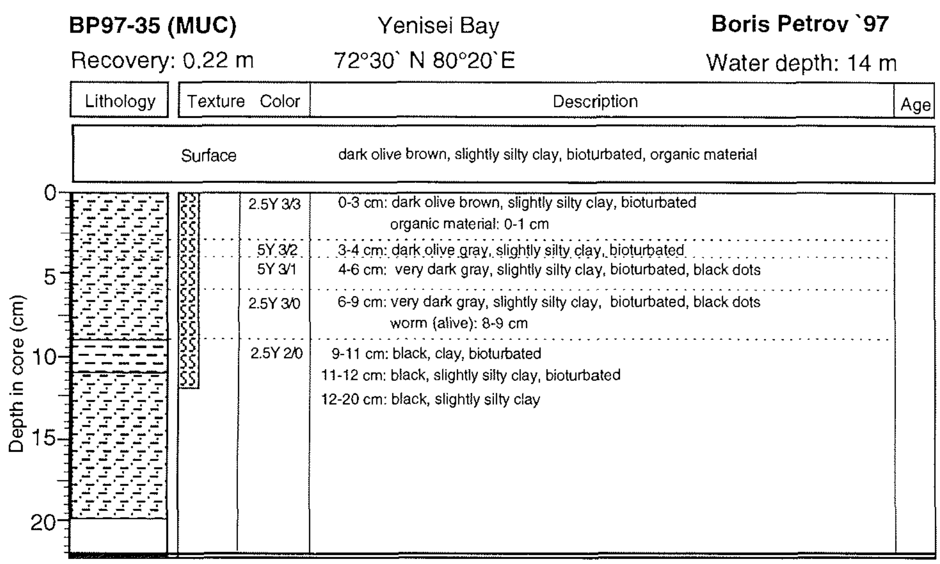


Fig. 6. Lithological columns of multi corer cores from stations BP97-10 in Ob Bay and BP97-35 in Yenisei Bay.

Results and Discussion

The distribution of Cs-137 in surface sediments (0-2 cm) is shown in Figure 2. The results confirm our previous interpretations about the significance of lithology of the surface sediments on the radioactivity level of Cs-137. Thus, muddy sediments with a larger sand content contain less cesium than sediments with high contents of clay which have a high sorption capability for Cs-137.

To a certain degree, this dependence is also observed in the distribution of Sr-90 (Kremlyakova et al., this volume). This relationship is not valid for the distribution of Pu-239,240 (Fig. 3). However, this may be caused by the low sample coverage in the estuarine areas.

We found a significant increase in the activity of radionuclide Cs-137 down-core in many sediment cores (Fig. 4). The concentrations of Cs-137 increase in 6-7 cm depth in sediment cores selected from Yenisei and Ob bays. The data can be well correlated with measurements on sediment cores taken in 1995 during the 22 cruise of the RV "Akademik Boris Petrov" (Fig. 5). If these data are compared with the description of the vertical structure of deposits (Fig. 6), it is clear that considerable vertical fluctuations of Cs-137 are not related to structural heterogeneity in a vertical section. These changes are most probably related to variable supply of radioactivity to the environment with time. It is assumed that this maximum of excess radioactivity is caused by the Chernobyl accident dating this level at 1986. This assumption is taking into account the published data on Chernobyl radioactivity in the Kara Sea and in the sediments of the surface outflow of the River Ob (Joint Russian-Norwegian Expert Group, 1992; Panteleyev, 1992). If our assumption is correct, the subsequent deposition of layers with less radioactivity allows to calculate the radioactivity fluxes to sediments in a certain time interval. Based on the data set of 1995 and 1997, we have estimated possible high sedimentation rates on the order of 0,5 cm/year. It is also interesting to note the presence of a second consider-able peak of activity at 15 cm depth in some sediment cores taken in Ob Bay (Fig. 4) that shows a significant supply of radionuclides in 1967, when one of the largest accidents occurred in the industrial site "Mayak".

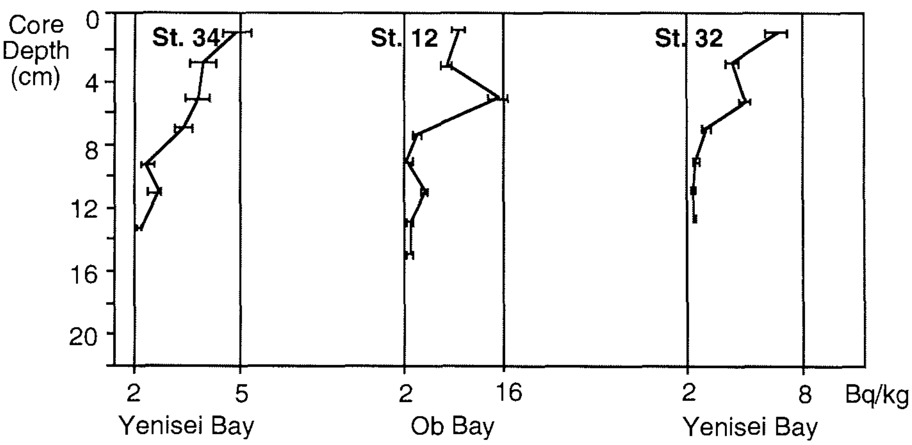


Fig. 7. Concentration of Sr-90 vs. depth in 1997.

The changes of Sr-90 with depth has a less pronounced character (Fig. 7), but nevertheless a correlation with vertical variations of Cs-137 is observed (correlation coefficient of 0.5). Future investigations will concentrate in part on investigations on concentrations of various radionuclides in the Ob and Yenisei estuaries and in part on developing a fast method of determination of ^{210}Pb for estimation of sedimentation rates.

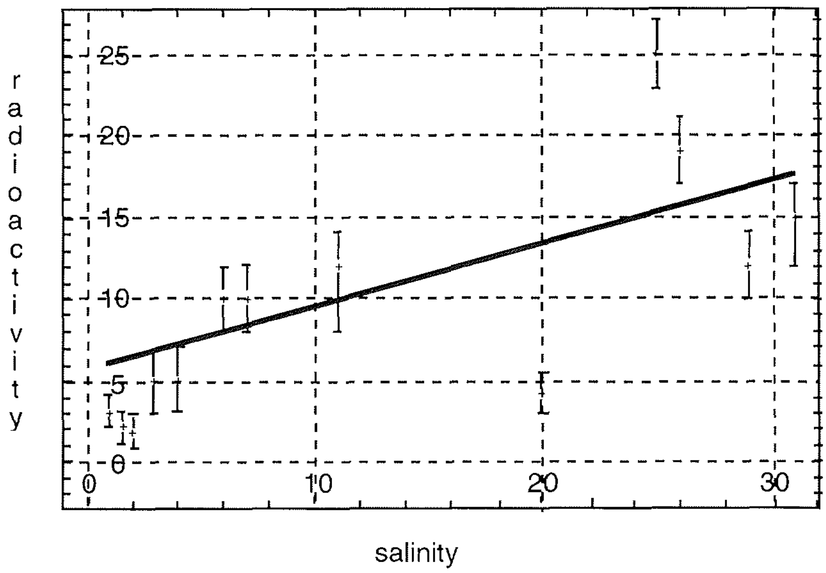


Fig. 8. Cs-137 concentration (dissolved) in samples as function of salinity.

The distribution of dissolved ^{137}Cs radionuclides in surface waters show that contents increase with increasing salinity (Fig. 8). We observed slight peaks in radioactivity of Sr-90 in the open part of the Kara Sea and Ob River, which, from our point of view, can be related to the influence of various sources, which contribute to a general radioactivity of the water in the investigation area despite of often changing synoptical and hydrological parameters.

Therefore, we performed a comprehensive radio-geochemical investigation in the southern part of the Kara Sea and the estuaries of Ob and Yenisei rivers. Observations were made at 59 stations. Distribution of Cs-137, Sr-90 and Pu-239,240 in the investigation area is irregular and its concentrations depend on lithological-geochemical factors, which proves the necessity to carry out a combined survey of artificial radionuclides and geochemical parameters.

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DETERMINATION OF RADIOSTRONTIUM IN SEA WATER AND BOTTOM SEDIMENTS FROM THE SOUTHEASTERN KARA SEA

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Introduction

The importance of radiostrontium determination in present ecosystems need not be discussed. The introduction of new radiochemical procedures for strontium isolation from environmental objects is of obvious analytical interest. Some combinations of precipitation, coprecipitation, solvent extraction and ion exchange are used. The most commonly used techniques are multi-step and time-consuming. Recently, extraction chromatographic methods are increasingly used in the analysis of samples from modern environments. The use of crown ethers to determine radiostrontium appears to be particularly promising (Zolotov et al., 1993). We developed a chromatographic method based on selective extraction of strontium with dicyclohexano-18-crown-6 ($DCH_{18}C_6$) (Kremlyakova, 1993). Chromatographic material is extracted in a macroporous copolymeric styrene-divinylbenzene matrix impregnated with a solution of $DCH_{18}C_6$ in tetrachloroethane (tvex). This "sorbent" is selective to strontium and has a proper capacity to it, which is of importance when analysing strontium-rich samples such as sea water. Moreover, this method allows to determine radiolead along with radiostrontium. It is a very important geochemical task because with knowledge of Pb-210 contents in geological samples it is possible to determine sedimentation rates (Kuznetsov, 1976). However, we do not present in this paper the data on Pb-210; this will be the subject of our next report.

Experimental

Samples of bottom sediments and sea water were analysed. The laboratory procedures of preparing extraction-chromatographic material and extraction chromatographic columns are described in Kremlyakova et al. (1990). We used a 10 % solution of crown ether in tetrachloroethane. The capacity of the resin exceeds 14 mg Sr /ml. To analyze bottom samples (25 - 50 g) we used chromatographic columns (d = 1 cm, l = 20 cm) with a total capacity of more than 80 - 100 mg. To determine Sr in sea water samples (50 l) we used larger columns (d = 4 cm, l = 20 cm) with a total capacity of Sr equal to 400 - 450 mg.

The pretreatment of bottom samples included the following steps: drying the samples at 102 °C until constant weight; calcination at 600 - 650 °C for 2 hours; leaching the residues twice with boiling 7.5 M nitric acid for 0.5 hours; acidic adjusting of extracts until 1.5 - 2.0 M/l HNO_3. Sea water was analyzed according to the following procedure: 50 l of sea water were heated up to 60 °C; a calculated quantity of sodium carbonate was added to sea water; the precipitate of alkaline earth elements was separated, air-dried and dissolved in nitric acid in order to have a concentration of 1.5 - 2.0 M/l HNO_3.

Table 1. Average concentrations of ions.

Element	µg	Element	µg	Element	mg	Element	µg
Ba	$7.5*10^2$	Mg	$>1.6*10^5$	Ti	$4.5*10^2$	K	$7.9*10^4$
Ca	$9.7*10^3$	Mn	$1.9*10^4$	V	$9.4*10^2$	B	$5.0*10^2$
Cd	5.6	Ni	$3.2*10^2$	Zn	$7.0*10^2$	Na	$7.5*10^5$
Cr	$3.4*10^2$	Pb	<0.025	Zr	$1.5*10^2$	Bi	<0.05
Cu	$3.1*10^2$	Sr	$7.4*10^2$	Co	$1.4*10^2$	Be	$2.1*10^1$
Al	$>2.8*10^5$	P	$8.8*10^3$	Fe	$>1.0*10^6$		

Nitric acid extracts of samples were passed through extraction chromatographic columns at a flow rate of 1.0 - 2.5 cm/min followed by washing through a column with 1.5 - 2.0 M/l nitric acid solution. Strontium and lead were desorbed with hot water at 60 - 70 °C. Lead was separated from Sr by precipitation of lead bromide or iodide and Sr was precipitated as strontium carbonate. In case of Sr-rich water samples we repeatedly passed strontium eluate adjusted by nitric acid to 1.5 - 2.0 M/l through the same column for two weeks after precipitation of Y-90 as yttrium oxalate.

Chemical yield of every step of analysis was checked by Sr-85, by the weight method or by the AES ICP method. A low background alpha-beta counting system UMF-M "Meteorit" was used for radiometric measurements. The ion content in nitric acid was determined with a IPAC 9000 "Jarell Ash" installation.

Results and Discussion

Nitric acid extracts of samples represent very saturated brines of macro- and microcomponents. Table 1 summarizes average concentrations of some ions in 50 ml of analysed solution resulting from a 20 g pretreated sample.

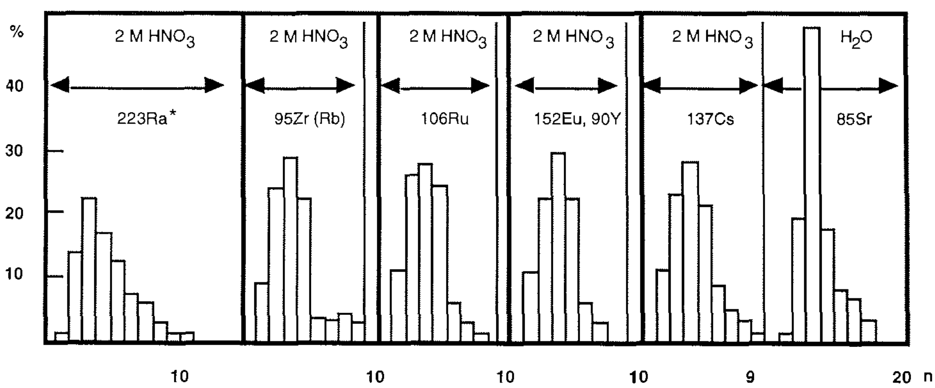

Fig. 1. Elution of interfering radionuclides through the extraction chromatographic column with tvex-$DCH_{18}C_6$; n - number of collectors, volume of collector is equal to 3 ml.

An additional point to emphasize is that sea water is enriched in Sr (8 mg/l), so that water samples contain up to 280 mg of Sr. Hence, the extraction chromatographic column contains a very huge load. Nevertheless, all interfering radionuclides are completely removed (Fig. 1) and Sr, Ba and Pb are selectively isolated, the Pb therewith is held better than Sr (in the absence of fresh radioactive fallout Ba need not be separated from Sr and Pb). The loss of strontium during the elution of solutions and following washing ranges up to 8 %, while Pb loss does not exceed 0.15 %. It is necessary to use 15 % tetrachloroethane solution of $DCH_{18}C_6$ to minimize strontium loss.

Table 2. Sr-90 content in bottom deposits.

Station	Place of sampling	Depth cm	Latitude N	Longitude E	Activity of Sr-90 Bq \ kg
12	Ob Bay	0 - 2	72°10′13.0″	74°17′37.0 ″	8.0 ± 0.8
		2 - 4			7.7 ± 0.8
		4 - 6			15.7 ± 0.1
		6 - 8			4.0 ± 1.0
		8 - 10			2.8 ± 0.7
		10 - 12			5.0 ± 0.4
		12 - 14			7.0 ± 0.8
		14 - 16			6.3 ± 1.0
18	Kara Sea	0 - 2	73°57′42.0″	76°08′19.8″	4.0 ± 0.8
21	Kara Sea	0 - 2	74°00′02.4″	81°00′27.6″	2.8 ± 0.3
32	Yenisei Bay	0 - 2	72°05′35.2″	81°28′52.2″	7.2 ± 1.0
		2 - 4			4.8 ± 1.0
		4 - 6			5.4 ± 1.3
		6 - 8			3.2 ± 1.0
		8 - 10			2.5 ± 0.7
		10 - 12			2.1 ± 0.2
		12 - 14			1.2 ± 0.2
		14 - 16			2.7 ± 0.5
34	Yenisei Bay	0 - 2	72°25′50.4″	80°24′25.8″	11.6 ± 0.1
		4 - 6			1.5 ± 0.1
		6 - 8			3.0 ± 0.3
		8 - 10			2.4 ± 0.3
52	Kara Sea	0 - 2			7.2 ± 1.5

The data obtained are presented in Tables 2 and 3. In general, they are not in conflict with results of other investigations, though it is difficult to compare different environmental data sets.

Table 3: Sr-90 content in sea water.

Station	Place of sampling	Latitude N	Longitude E	Activity of Sr-90 Bq \ m³
1	Ob Bay	73°54´38.0´´	73°10´59.0´´	4.8 ± 0.4
12	Ob Bay	72°10´13.0´´	74°17´37.0´´	12.2 ± 0.9
19	Kara Sea	74°00´02.4´´	79°01´28.4´´	2.9 ± 1.2
24	Kara Sea	73°32´04.2´´	79°55´16.2´´	6.0 ± 1.2
32	Yenisei Bay	72°05´35.4´	81°28´52.2´´	1.2 ± 0.5
42	Kara Sea	´73°53´57.6´	81°40´01.2´´	1.2 ± 0.5
47	Kara Sea	72°35´00.6´	73°44´54.6´´	4.2 ± 0.6
55	Kara Sea	73°13´27.9´	75°37´08.4´´	2.9 ± 0.5
64	Kara Sea	71°03´05.0´	50°24´09.0´´	2.0 ± 0.6

Thus, the method allows simultaneous determination of radionuclides of strontium and lead with reasonable simplicity which is important for geoecological investigations.

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TRACKING AND DISTRIBUTION OF RADIOACTIVE CONTAMINATION FROM NUCLEAR PLANTS TO THE BOTTOM SEDIMENTS OF THE OB AND YENISEI RIVERS AND THE KARA SEA BASIN

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Abstract

In the course of the joint Russian-German expedition to the Kara Sea, Ob and Yenisei estuaries in August-October 1997 sediment cores were taken at 27 stations. The first results of the investigations on samples from 8 stations demonstrate a strong variability of artificial ^{137}Cs distribution in the sediments of the Ob and Yenisei estuaries. Geochemical investigations of sediments revealed that characteristic groups of trace elements allow to distinguish sediments formed in the Ob and Yenisei rivers.

Introduction

Radioecological conditions of the Kara Sea are determined by the effect of various radioactive contamination sources: tests of nuclear weapons on the Novaya Zemlya Islands, discharge of liquid radioactive wastes to the sea, dumping of containers with radioactive wastes and used-up reactors of submarines and global fall-out of radionuclides from the atmosphere since 1945.

Of major importance is the supply of radioactivity with waters of the great Siberian rivers Ob and Yenisei. In the upper course of these rivers warhead plutonium producing plants, nuclear reactor manufacturing plants and nuclear fuel processing plants are located: namely, PA Mayak in Chelyabinsk-65 (Techa River), Sibirsky Chemical Operations in Tomsk-5 (Tom River) and Mining and Chemical Operations in Krasnoyarsk-45 (Yenisei River).

Within the framework of the project "The Nature of Continental Run-off from Ob and Yenisei Rivers and its Behaviour in the Adjacent Arctic Basin Kara Sea", it is important to study the processes of spreading of river sediments and associated radioactive contamination in the mixing zone of riverine fresh water and sea water and in the adjacent Kara Sea.

Investigations of geochemical characteristics of bottom sediments formed by material from various sources, along with other methods will allow to identify the sources of radioactive contamination which are located both inside and possibly outside the zone of mixing.

Here we describe the first results of our investigations on material collected at stations 1, 8, 9, 10, 12, 30, 31 and 32 during the 28th cruise of the RV "Akademik Boris Petrov" (Fig. 1).

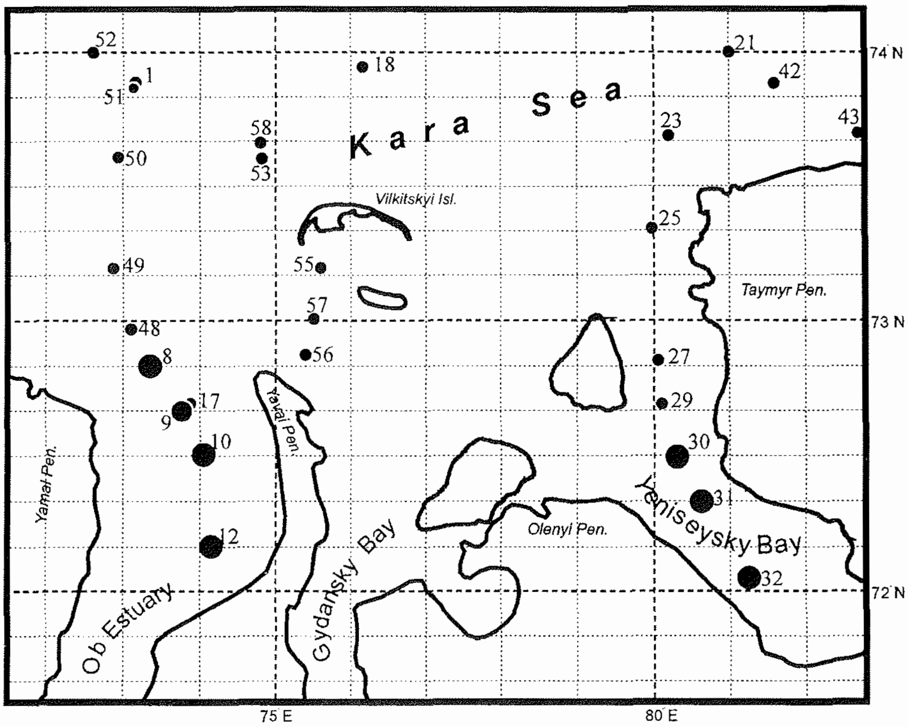

Fig. 1. Locations of the sampling stations. Stations, which are used in this study are marked with a large dot.

Methods

Radionuclides ^{137}Cs and ^{40}K were measured in dried samples transferred into a cuvette, for which the geometrical coefficients were determined before. Non-destructive analysis was applied using a gamma-spectrometer with the Ge (Li) semiconductor detector DGDK-125 and the 8000-channel amplitude analyser SBS-40. The exposure time was about 50000 sec. The equipment and standards were checked by GOSSTANDART of the Russian Federation. The analysis was performed in the All-Russian Research Institute for Geology and Mineral Resources, St. Petersburg, Russia.

Chemical elements were determined by instrumental neutron-activation analysis (INAA) in the Institute for Ore Deposits Geology, Mineralogy, Petrography and Geochemistry (IGEM) in Moscow. As standards, the rock and ore compositions BIL-1, BIL-2, RUS-4 (Russia), KH, GM, TB, BM (Germany) and SL-3 (IANE) were used. Samples and standards have been irradiated for ten hours in neutron flux of $2.3*10^{13}n/cm^2*sec$.

The induced activity was measured simultaneously by the two gamma-spectrometers:

1. NUC-8100+DGDK-50V (coaxial Ge(Li) detector, measuring energy range is 100-1800 KeV, resolution is 2.3KeV on the line 1332 KeV).

2. NUC-8100+BDRG (planar detector made from ultrapure Ge, measuring energy range is 50-160 KeV, resolution is 550 eV on the line 212.8 KeV.

Chemical element contents and detection limits were determined in two stages: on the 7th-10th day after irradiation (Na, Ca, As, Rb, Mo, Ba, La, Nd, Sm, Lu, W, Au, U) and on the 25th-30th day after irradiation (Sc, Cr, Fe, Co, Zn, Se, Sr, Ag, Sb, Cs, Ce, Eu, Tb, Yb, Hf, Ta, Hg, Th).

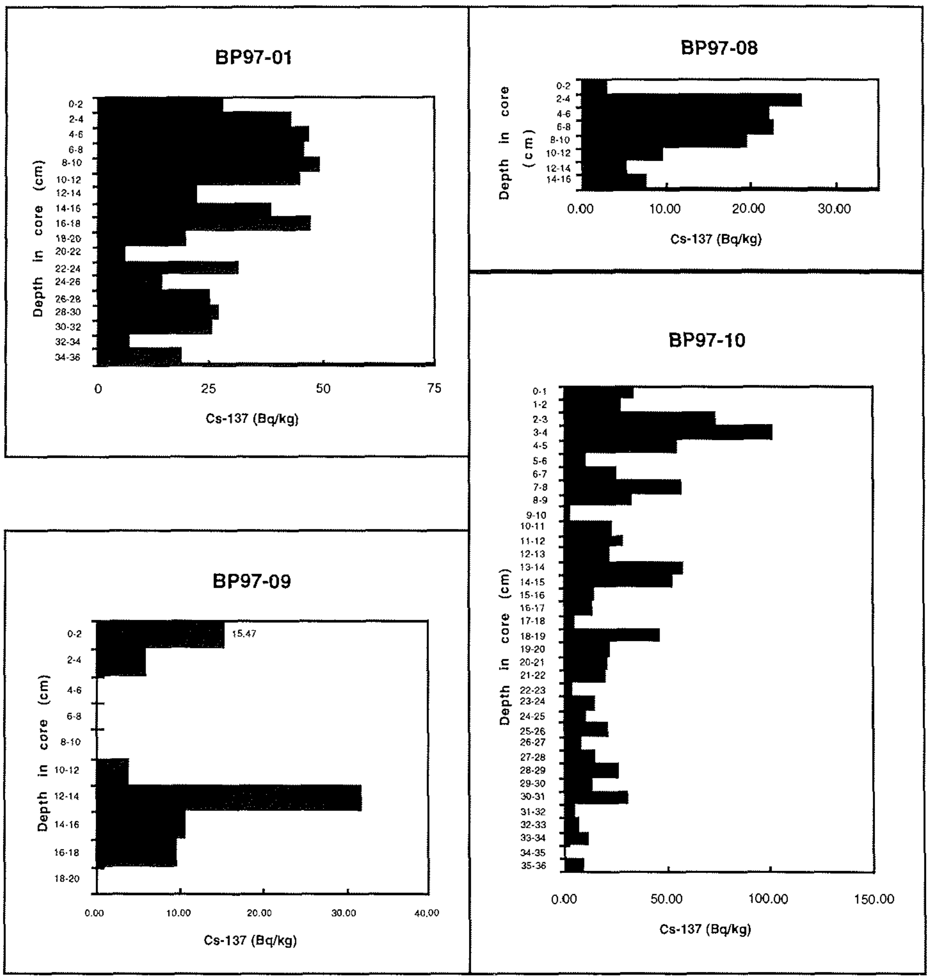

Fig. 2a. Vertical distribution of ^{137}Cs in bottom sediments (Stations 1, 8, 9, 10).

Results

Distribution of ^{137}Cs in sediment sections is shown in Figures 2a and 2b. Previous investigations revealed distinct differences in its distribution in bottom sediments of the Kara Sea in general and in the estuary of Yenisei, in particular in the upper 4-9 cm (Galimov et al., 1996). Our new data obtained on cores taken from the upper 30-40 cm of sediments support this conclusion in general. However, along with higher radioactivity with increasing depth in the upper 10 cm in sediments from the Yenisei, a substantial increase (up to 40 Bq/kg) in the interval of about 18-30 cm (St. 30, 32) was discovered (Fig. 2b).

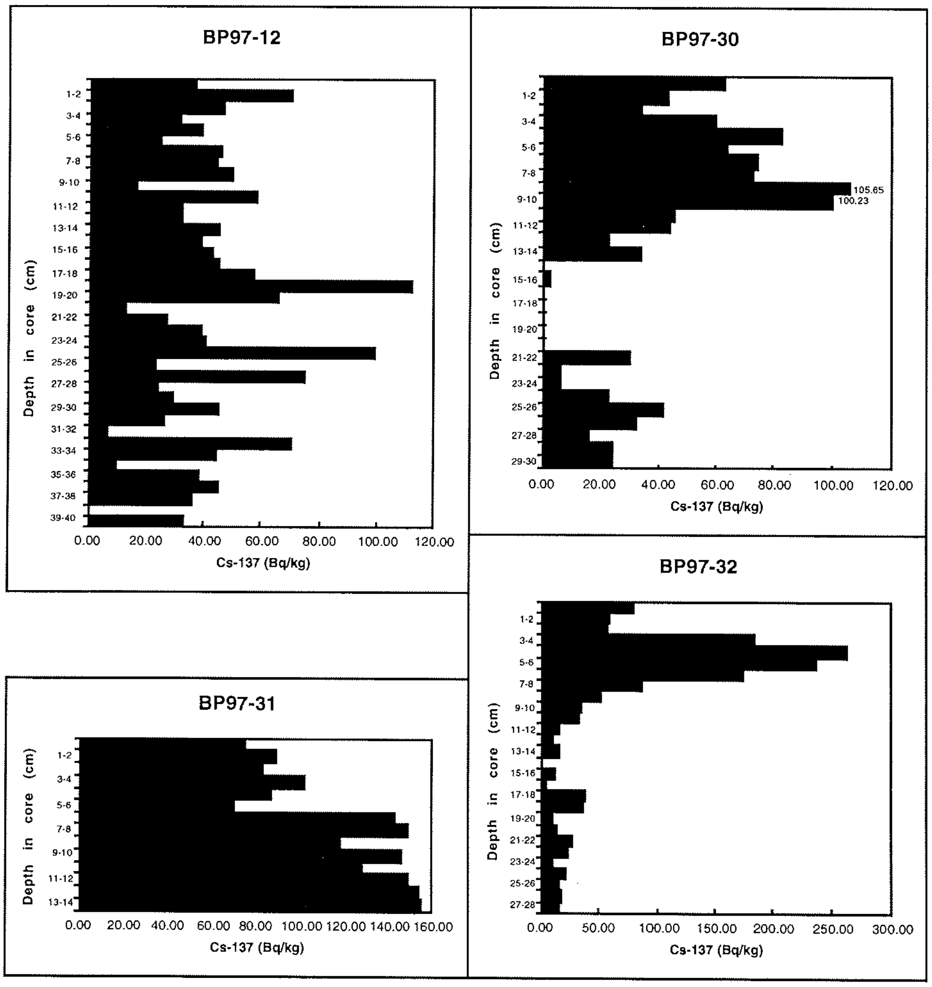

Fig. 2b. Vertical distribution of ^{137}Cs in bottom sediments (Stations 12, 30, 31, 32).

The difference in geochemical characteristics of various bottom sediments of Ob and Yenisei estuaries was described by comparative analysis of the first two statistical parameters of the distribution of chemical components in the sediment samples. The data of Ob Estuary consisted of samples from stations 8, 9, 10 and 12 (72), while the data of Yenisei Estuary consisted of samples from stations 30, 31 and 32 (72). Each sample was analysed for 23 trace elements (data are shown in ppm), three major elements (calculated as oxides in weight %), as well as ^{137}Cs and ^{40}K isotopes (Bq/kg). Zero values were replaced by those of the detection limit of the analytical method. Table 1 shows mean, minimum and maximum values of element contents and their standard deviations.

Tab. 1. Mean, maximum, minimum and standard deviations of chemical element contents in Ob and Yenisey samples.

	Ob´ Estuary				Yenisei Estuary			
Elements	Mean	Min. Value	Max. Value	Std. Dev.	Mean	Min. Value	Max. Value	Std. Dev.
Cs137(Bq/kg)	31.41	0.09	112.41	24.79	59.01	0.09	263.37	58.43
K40 (Bq/kg)	542.29	99.99	979.67	201.04	523.89	151.36	1203.06	192.73
Fe2O3 %	9.78	6.45	11.83	1.22	7.88	5.96	10.18	1.15
CaO %	1.64	0.33	3.16	0.71	4.44	2.93	6.17	0.74
Na2O %	3.03	2.30	4.91	0.54	3.17	2.31	4.56	0.49
Br	76.20	35.00	172.30	26.71	35.41	11.00	65.00	14.55
Ba	396.23	77.00	655.00	119.23	375.54	56.60	616.20	121.73
As	29.04	0.90	57.80	17.79	8.66	3.50	205.30	25.21
Sb	1.23	0.64	5.36	0.56	0.79	0.15	3.44	0.63
Sr	166.79	79.10	575.10	143.18	297.05	78.90	643.00	160.22
Rb	96.18	58.40	147.10	20.45	69.12	27.30	111.90	17.75
Cs	6.00	3.82	7.91	0.78	3.13	1.79	4.73	0.76
Sc	16.25	12.20	18.80	1.52	19.48	16.10	23.00	1.99
Cr	101.08	82.30	118.70	8.41	109.29	91.10	127.80	9.33
Co	25.83	17.30	30.30	3.03	26.15	19.50	33.80	3.66
Ag	2.42	0.75	4.48	0.99	3.79	1.11	6.35	1.24
La	35.58	29.80	42.10	2.76	26.24	19.70	34.30	3.67
Ce	63.95	51.00	72.10	5.02	48.34	36.60	60.90	6.74
Nd	30.42	22.40	37.80	3.59	25.65	19.20	32.90	3.53
Sm	6.08	4.97	7.02	0.45	5.31	4.13	6.57	0.64
Eu	1.46	1.23	1.70	0.11	1.34	1.02	1.60	0.14
Tb	0.90	0.64	1.12	0.12	0.79	0.50	1.29	0.16
Yb	2.96	2.46	3.58	0.25	2.84	2.26	3.94	0.37
Lu	0.51	0.36	0.64	0.06	0.43	0.33	0.56	0.06
Hf	4.23	3.24	6.53	0.76	4.81	3.75	6.02	0.45
Ta	0.82	0.67	1.04	0.08	0.75	0.55	0.96	0.11
Th	9.24	6.84	10.80	0.88	6.56	4.35	8.63	1.16
U	2.14	1.02	3.74	0.55	1.13	0.21	1.97	0.35

To demonstrate more clearly the existing variance, the data are shown in Figure 3 as logarithms of the relation of mean and standard deviations of element contents in sediments of the Ob and Yenisei estuaries. A 1.5- and 2-fold difference corresponds to an absolute value of 0.4 and 0.69 natural logarithms. Thus, the samples from Ob and Yenisei differ by a factor of more than 1.5 in mean values of ^{137}Cs, CaO, Br, As, Sb, Sr, Cs. Ag, U and in standard deviations of ^{137}Cs, Br, Hf, U, as well as by nearly 1.5 in mean values of Rb, La, Ce, Th and in standard deviations of As, La, Ce, Sm, Yb, Ta. However, the major part of the measured As and Sb contents are below the detection limit.

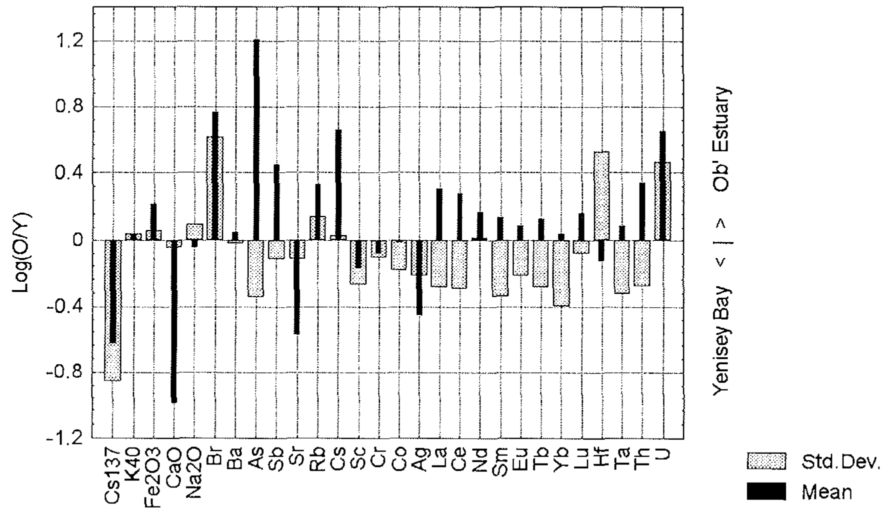

Fig. 3. Relation between the mean and standard deviations of chemical element contents in Ob and Yenisey samples.

The geochemical variance can be demonstrated in more detail in histograms of element distributions. For example, Figure 4 shows histograms of the distribution of selected elements which differ most greatly, together with a histogram of ^{137}Cs isotopes. Grey colour and "O" symbol mark the distributions in Ob samples, while black colour and "Y" symbol mark those in Yenisei samples. It is clearly seen that a substantial difference in mean values of ^{137}Cs concentrations is reflected in several samples from the Yenisei with abnormally high concentrations of this artificial isotope, while its background distributions are rather similar. Excessive concentrations of natural Cs isotopes, as well as of other elements listed above were not practically registered. However, their background distributions differ greatly primarily in a clearly demonstrated shift of their centres. The form of concentration distributions is close to a normal one for all natural components under consideration in Ob samples. In Yenisei samples components such as Fe_2O_3, La, Ce, Th clearly demonstrate the polymodality of their distribution (A polymodal form of distribution is expected for ^{137}Cs, and it is more brightly indicated in the Yenisei samples, as compared to those from Ob).

Discussion

Identification of the absolute age of the bottom sediments in the lower reaches of Ob (in the area of the town of Labytnagi) performed by Dr. H.D. Livingston and Dr. F.L. Sayles in WHOI showed that the average annual rate of sediment accumulation ranges from 0.5 to 0.8 cm. If we assume that sediment accumulation rates in the Ob and Yenisei estuaries are lower, then the difference in time required for the formation of the upper and lower intervals of ^{137}Cs peak concentrations will not exceed 20 years. The half-life of ^{137}Cs is estimated at

30,17 years. Thus, the radioactivity level of ^{137}Cs in the lower interval can be estimated at 60 Bq/kg.

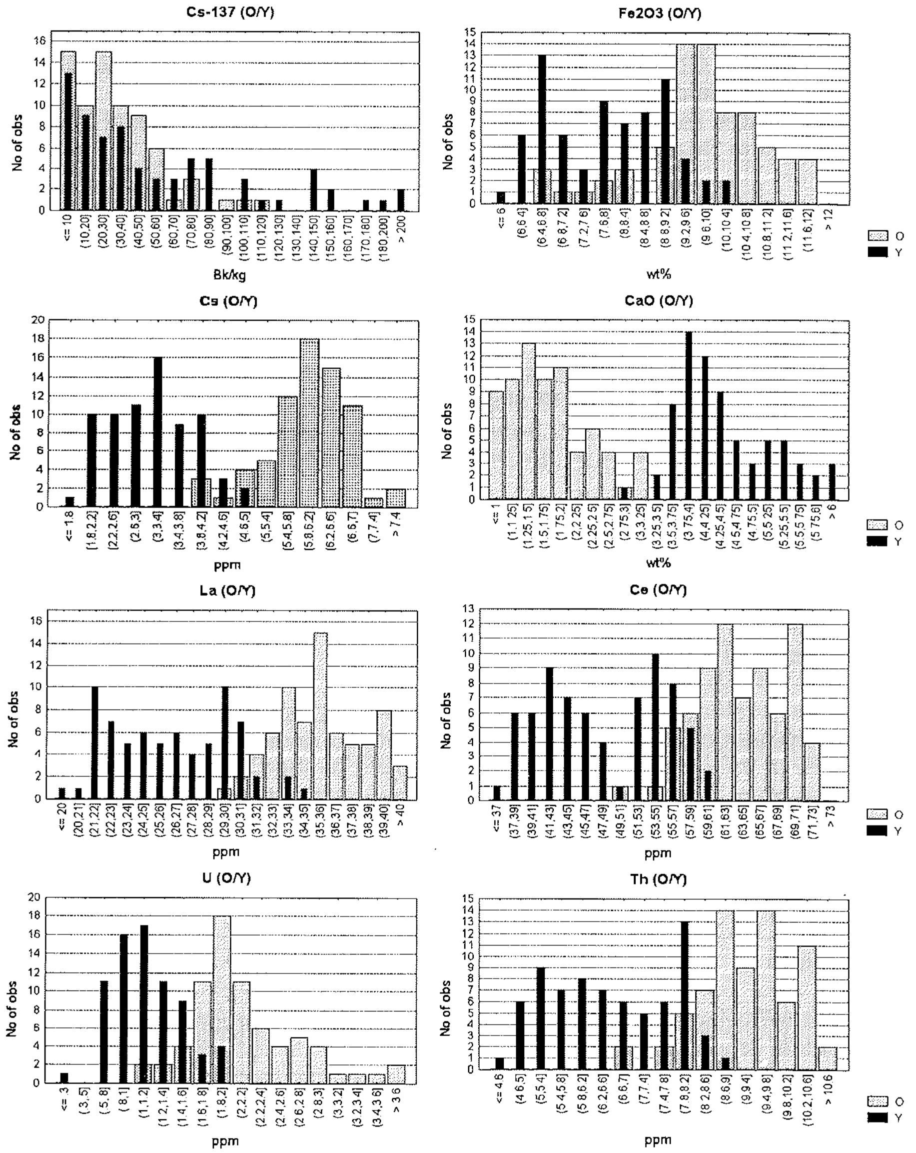

Fig. 4. Histograms of chemical element distributions in Ob and Yenisey samples.

The main difference between the sediments of the Yenisei and Ob estuaries in the vertical distribution of ^{137}Cs is the more even and gradual increase and decline of element contents with increasing depth in the Yenisei and their substantially higher concentrations (up to 260 Bq/kg). Probably, this difference can be explained by the fact that the mineral composition of bottom sediments in the investigation area is not uniform. In the sediments of the Yenisei Estuary high contents of clay minerals and a lower variability of lithologies increase the sorption capacity. However, the clearly demonstrated geochemical heterogeneity of the Yenisei sediments with their lower lithological variability as compared to the Ob sediments may reflect differences in geological and geochemical conditions in the areas of continental run-off from the Yenisei River basin. If it is really so, the identification of sediments of Yenisei and Ob origin in the Kara Sea might be a more complicated task.

Conclusions

1. Bottom sediments of the Yenisei estuary are more liable to substantial contamination with ^{137}Cs, than those of the Ob estuary.

2. Bottom sediments of the Ob and Yenisei estuaries along the transects of stations 8-9-10-12 and 30-31-32 clearly differ in geochemical characteristics which are determined by the peculiar geology of the run-off areas and probably by the difference in the hypergene conditions of sediment accumulation.

3. Polymodality in the distribution of some elements, which is characteristic of the Yenisei samples shows the heterogeneity of the material accumulated in the bottom sediments. This can be explained by the variation of geological characteristics of the run-off areas or by mixing of sediments from the Yenisei with sediments of other origin.

4. After the evaluation on the basis of statistically more representative data and development of efficient application methods the discovered geochemical separability of the sediments, which are supplied by the Ob and Yenisei rivers, may become an instrument for tracing sediments of various origin to the area of their complete mixing. Accordingly, predicting the distribution of artificial radionuclides associated with solid particles of the Ob or Yenisei catchment areas appears possible.

Future work

Today, the following work on the collected material is in progress according to the analytical programme:

- measurement of the concentration of artificial radio nuclides;
- identification of the mineral composition of sediment layers;
- statistical analysis of the results of bottom sediment analyses taken at all other stations (including those, which were taken in the course of the 22th cruise of the RV "Akademik Boris Petrov" in 1995);
- development of methods for the identification of differences between sediments of various origin by numerous features, first of all by geochemical characteristics;
- compilation of a map with the distribution of sediments of Ob and Yenisei origin, with the identification of the possible borderline of the zone of their complete mixing on the basis of the processed data from all the stations.

Acknowledgements

The authors kindly appreciate the contribution of A.D. Krasnuk (VNIIOkeangeologia), who carried out ^{137} Cs content measurements; A.L. Kerzin (IGEM), who conducted the measurements with INAA; G.A. Nadiyarnykh (IGEM) for thoroughly preparing specimens for all types of analysis. We are rather grateful to Dr. V.N. Lukashin, Dr. J. Matthiessen and Dr. O.V. Stepanets for their assistance and support, as well as to all the members of the expedition and crew of the RV "Akademik Boris Petrov" who took part in the 28th cruise.

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SEDIMENTOLOGY

AND

INORGANIC GEOCHEMISTRY

SUSPENDED PARTICULATE MATTER IN THE OB AND YENISEI ESTUARIES

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Introduction

Investigations in the Arctic Basin are becoming a priority task of the world scientific community because the Arctic Ocean plays an important role in regulating the global climate (e.g. Herman, 1989). The Kara Sea is the second largest shelf sea of the Arctic where the Ob and Yenisei rivers (the greatest rivers of the Russian Arctic) discharge large quantities of dissolved and suspended matter (Gordeev et al., 1996).

Despite of the importance of these rivers in transporting sedimentary material into the Arctic Basin, previous investigations dealt mainly with the chemistry of the river particulate and dissolved matter and few studies dealt with composition of the material (Dai and Martin, 1995; Jambers et al., 1997; Lisitsyn and Vinogradov, 1995; Shevchenko et al., 1996, 1997). Investigations in estuaries are of special interest because they are the main part of the marginal filter where the fresh water of rivers mix with the salt water of the shelf seas. A number of physical and chemical processes control the transfer of matter from the river system to the sea resulting in sharp changes in the composition of the dissolved and suspended particulate load (Lisitsyn, 1995). The major goal of the present work is to expand our knowledge about the composition of suspended particulate material transported by the rivers into the mixing zone and to study its transformation at the river-sea barrier.

Materials and Methods

The material for this study was obtained during the joint Russian-German expedition with RV "Akademik Boris Petrov" in the Kara Sea and the estuaries of the Ob and Yenisei rivers in September 1997. During the expedition the water column was sampled for suspended particulate material at 21 stations. Data from 13 stations are presented in this publication - 7 stations (27 samples) from the Ob Estuary and 6 stations (24 samples) from the Yenisei Estuary. The locations of these stations are shown in Figure 1, the geographic coordinates and depths of the water sampling are presented in Appendix 1.

During the expedition sampling was carried out on anchor stations. Before sampling the water column was sounded by a CTD probe which continuously measured water pressure, temperature, conductivity and dissolved oxygen content, and the water column sampling was planned according to these results. Usually we chose four depths: the sea surface (0 m), the depth just above the pycnocline and below the pycnocline, and ca. 1-2 m above the sea bottom.

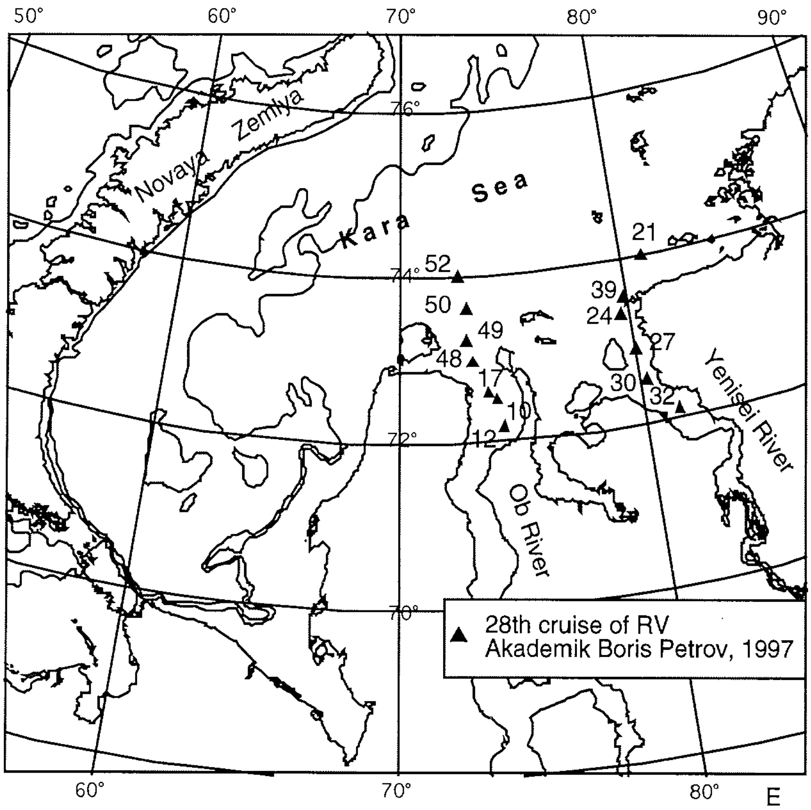


Fig. 1. Location of suspended matter sampling stations.

The water samples were collected using a rosette sampler with 24 Niskin bottles (1.8 l). The rosette was lowered to the deepest sampling depth and 5-6 bottles were closed, then the rosette was lifted to the next horizon for sampling and so on up to 0 m. After the rosette sampler returned onboard 6-9 l of water were filled in special prepared clean bottles and filtered under vacuum through preweighted Russian nuclear pore filters with a diameter of 47 mm and a pore size of 0.45 µm using Millipore filterholders. Each sample was filtered through three filters: two - nuclear pore filters (ca. 0.5-1.5 l), one - through precombusted Whatman GF/F glassfiber filters for determination of particulate organic carbon (POC) and its composition (ca. 2-5 l). After filtration filters were washed with distilled water, dried at 60°C and packed for later analysis in the P.P.Shirshov Institute of Oceanology, Russian Academy of Sciences (IORAS).

In the institute the nuclear pore filters were weighted and suspended matter concentrations were determined. Afterwards the filters were used for different analyses. One nuclear pore filter was used for preliminary assessment of the particulate matter composition and sizes of the particles by electronic microscopy. A small part of this filter was used to study morphology and grain sizes of particles and qualitative elemental composition of selected individual particles by the scanning electron microscope SEM-515 with X-ray microprobe EDAX PV9900 (Philips, USA) in the Alfred Wegener Institute (AWI). The grain-size analysis was carried out with another part of the filter using the laser analyser GALAI SIS-1 in AWI.

The second nuclear pore filter was analysed at VNIIOkeangeologia by XRF-method with the scanning spectrometers SPARK-1 and SPARK-2. The first part was used for determination of Ti, Ba, V, Cr, Mn, Co, Fe, Ni, Zn, As, Pb and Sr, the second - for Si, Al, P and Ca. The error of analysis of macroelements was 3%, for microelements up to 10%. The results were normalized to external standards. The following Russian standards of bottom sediments were used: SDO-1 (terrigenous clay), SDO-2 (volcano-terrigenous ooze), SDO-8 (siliceous ooze), SDO-9 (deep-sea red clay) which were elaborated in IORAS (Berkovits and Lukashin, 1984; Arnautov, 1990).

Contents of the biogenic amorphous silica (opal, Si_{am}) were calculated with the terrigenous matrix method using an average ratio of Si/Al for terrigenous sedimentary rocks and the contents of Si and Al in the samples. Opal contents were calculated using the average ratio Si_{am} = Si - Al * 3.2, where Si and Al are the contents of these elements in the sample, and 3.2 is an average value of Si/Al ratio in sedimentary rocks on the Earth (Ronov and Yaroshevsky, 1967).

A quarter of the glassfiber filter was used for determination of particulate organic carbon (POC) by the coloumetric method in IORAS. Another part will be analysed for the stable carbon isotope composition of organic matter in the V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry.

All measurements are listed in Appendix 1 as concentrations (µg/l) and contents (%). The general characteristics of the suspended matter as well as the distribution of seleted components and elements are described below.

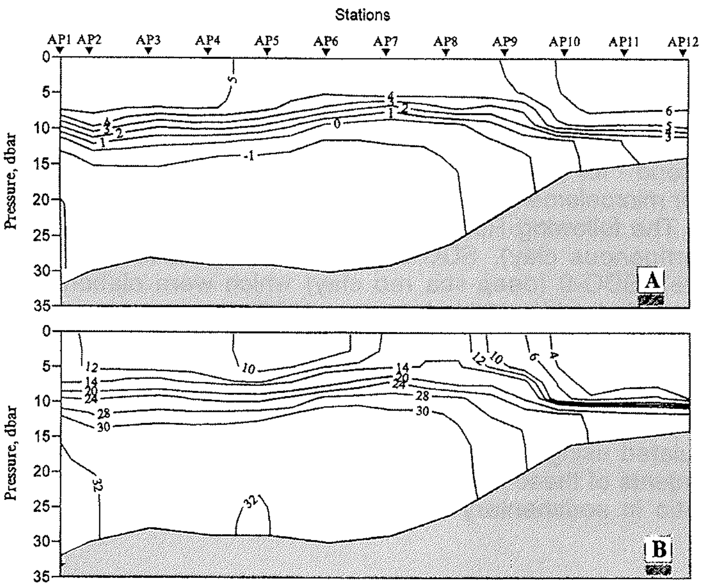
Results and Discussion

Structure of the water column

Figure 2 shows the distribution of temperature and salinity on transects along the Ob and Yenisei estuaries (Churun and Ivanov, 1998). The water column in the Ob Estuary consists of two layers: the upper layer has a thickness of 5-8 m (T = 4.5 - 6 °C, S = 3-12 $^{o}/_{oo}$); the lower layer lies between 12-30 m and consists of sea saline water with negative temperatures. The strong pycnocline has a thickness of 7-8 m and very high gradients of temperature and salinity.

The water column of the Yenisei Estuary also consists of two layers: the upper one has a thickness of 6-8 m (T = 6 - 8 °C, S = 1.9 -11.87 $^{o}/_{oo}$), and the lower layer which is comparable with the Ob Estuary lower layer, located at 19-40 m, consists of sea water with a salinity of more than 30 $^{o}/_{oo}$ and a negative temperature less than -1°C. In the southern part of the transect south of 72°35'N, the river water occupies the whole water column. There the salinity is less than 1.9 $^{o}/_{oo}$ and temperature increases up to 8.01°C. Brackish water was found near the sea bottom (Churun and Ivanov, 1998).

Ob Estuary



Yenisei Estuary

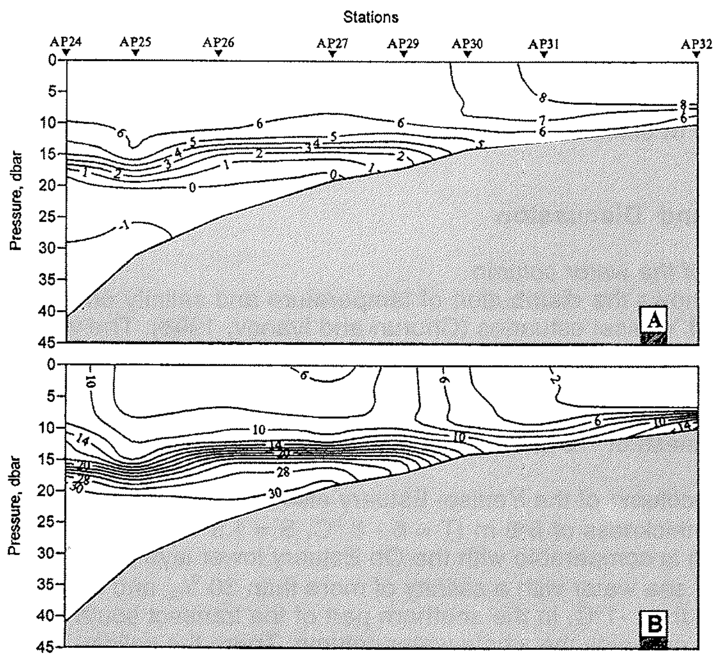


Fig. 2. Distribution of temperature (A) and salinity (B) on the transects of the Ob and Yenisei Estuary.

Approximately the same hydrographic situation was observed in these parts of the estuaries in September 1993 during the 49th cruise of RV "Dmitry Mendeleev" (Burenkov and Vasilkov, 1995). Thus we have an extensive mixing zone spreading over more than a hundred km and the processes of transformation of river matter likely occurs along the whole length of our transects.

Composition of particulate matter

Investigation of the samples using electronic microscopy revealed that the composition and grain size of the suspended particulate matter changes substantially from the southern to the northern parts of the transects in both estuaries. On the southern stations (St.12 in Ob Estuary and St. 32 in Yenisei Estuary) the grain size of the suspension ranges from <1 to 70-80 μm in the whole water column. EDAX analyses showed that mineral particles consist of quartz and alumosilicate minerals (Figs. 3a,b). Besides Si and Al, EDAX spectrograms display the presence of K, Na, Mg, Fe, Ti. Moreover the relations between these elements vary in the different particles (Fig. 3).

Samples from the Ob Estuary (St. 12 and 10) contain particles of Fe-alumosilicates (Fig. 3c) and from the Yenisei Estuary (St. 32) Ti-alumosilicates (Fig. 3d). High contents of Ti-rich particles have been already found in suspended matter from the Yenisei Estuary collected in 1993 during the 49th cruise of R/V "Dmitry Mendeleev" (Jambers et al., 1997). Some large diatoms (up to 200μm) and large aggregates of organic matter occurred together with the mineral components. Further north large particles disappear above the pycnocline but aggregates of thin spherical particles with sizes from <1 to 2 μm appear. EDAX analysis of these particles showed that they are weakly crystalline and composed of alumosilicates (Fig. 3d). The spherical particles are especially numerous in the Ob and Yenisei estuaries at stations 17 and 27, respectively. Such spherical particles increase in abundance northward and are found everywhere. Particles containing Ca and P together with Si and Al were also observed (Fig. 3f). In the northern part of both estuaries the particle contents on the filters decrease and the size of the mineral particles does not exceed 5-7 μm. Besides of the spherical objects, irregular particles were found which are mainly quartz and alumosilicates. Amorphous particles with high contents of Fe and Mn sometimes containing Si and Al were observed (Fig. 3g-i). Apparently they are amorphous Fe-siliceous gels and Fe- and Mn-oxyhydroxides, which are formed usually in zones of saline and fresh water mixing (Sholkovitz, 1976; Turner, 1996). Everywhere on both transects diatoms are present, their numbers increasing towards the Kara Sea. Many aggregates of organic matter and organic films covered the pores of filters. The organic films are destroyed with X-rays.

During EDAX analysis some particles containing gold were found. The particles with Au occurred mainly in the zones of intensive mixing (St. 10 - Ob Estuary and St. 30 - Yenisei Estuary) but they were also found in the open sea. As a rule they have irregular forms and different sizes. Such particles are absent in samples from the southern edges of the transects. Particles with a size of about 1 μm are more abundant, although grains with sizes of 30 and even 60 μm were found at St. 10. The size of particles with Au do not exceed 10 μm in the Yenisei Estuary. Such large particles do not occur in the northern

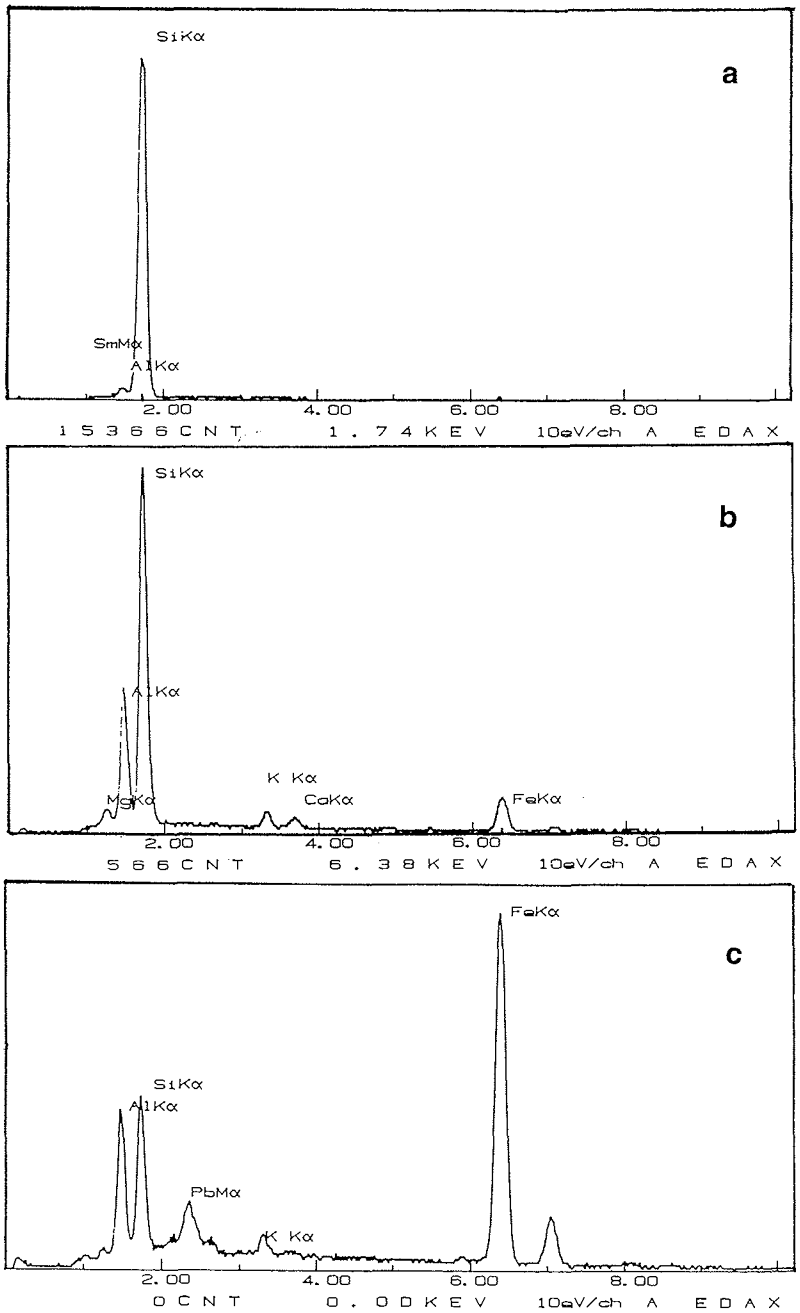


Fig. 3. Spectrograms of X-ray microprobe EDAX analysis.
a - quartz particle, 10 μm (St. 10, 0 m);
b - the most common alumosilicate, 3 μm (St.12, 8 m);
c - Fe-alumosilicate, 1.5 μm (St. 10, 0 m);

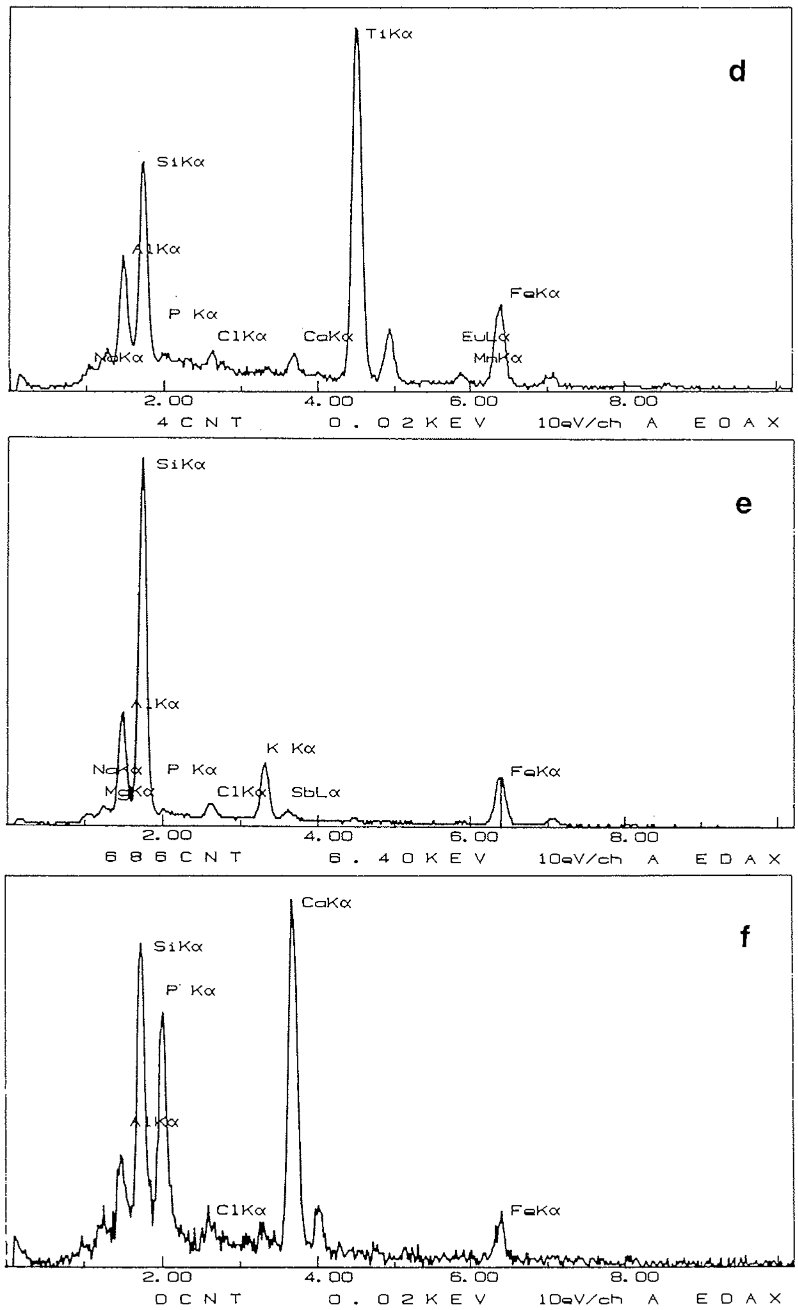


Fig. 3 (cont´d). Spectrograms of X-ray microprobe EDAX analysis.
d - Ti-alumosilicate, 2 μm (St. 32, 5 m);
e - spherical particle typical for the mixing zone, 2 μm (St. 17, 5.5 m);
f - amorphous Ca-P-alumosilicate particle, 3 μm (St. 30, 12 m);

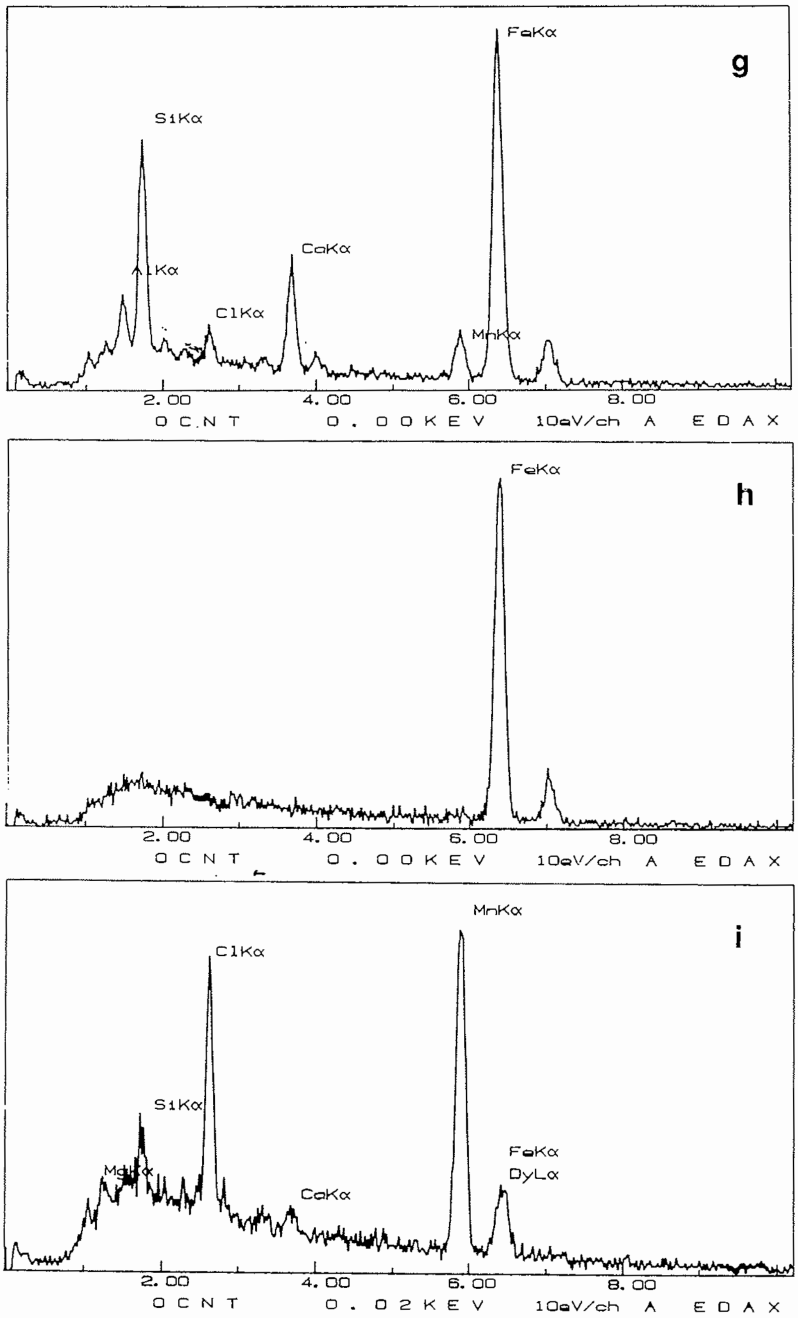


Fig. 3 (cont´d). Spectrograms of X-ray microprobe EDAX analysis.
g - amorphous Fe-alumosilicate particle, 4 µm (St. 24, 12 m);
h - Fe-oxyhydroxide, 1 µm (St. 21, 10 m);
i - Mn-oxyhydroxide, 3 µm (St. 52, 7 m).

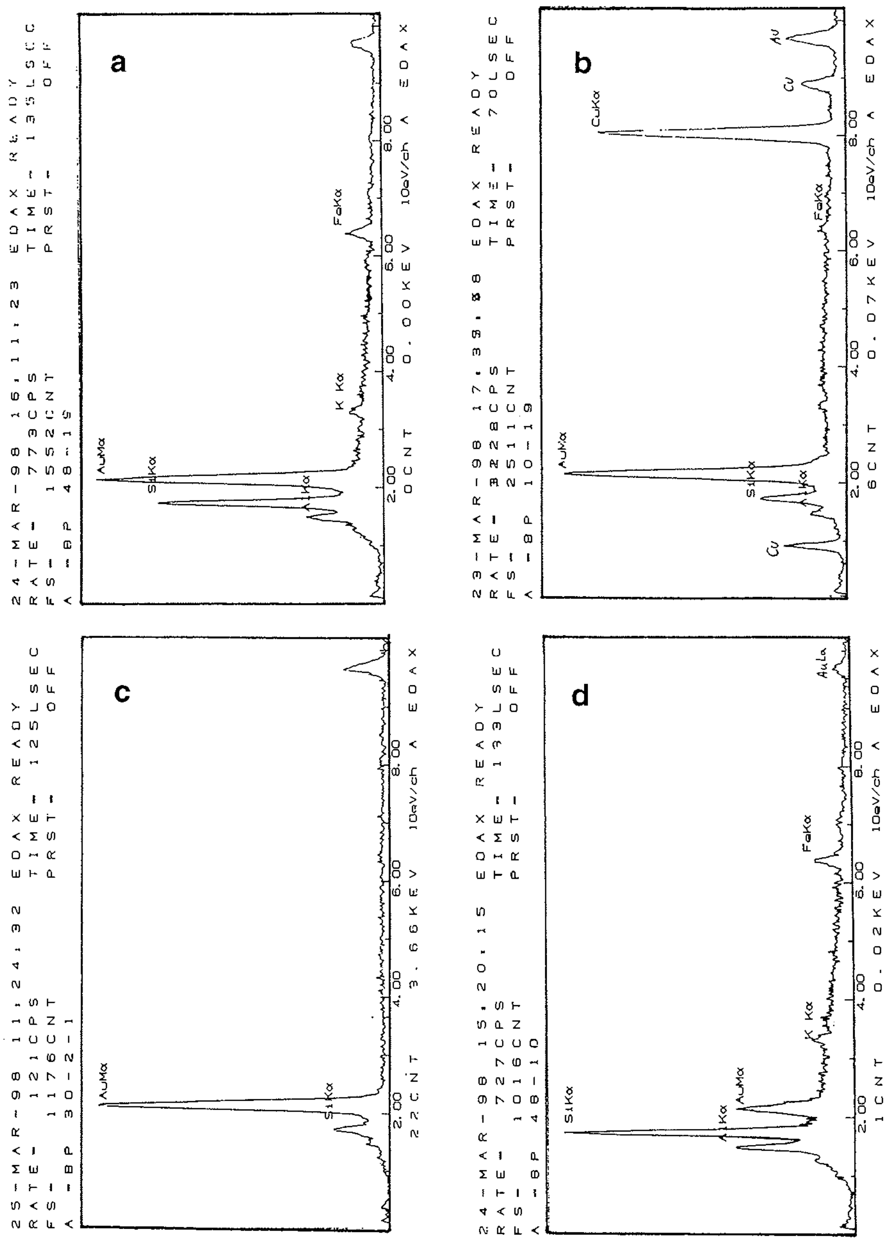


Fig. 4. Spectrograms of X-ray microprobe EDAX analysis: Gold particles from the mixing zones.

a - Ob Estuary, 0.3 μm (St. 48, 7 m);

b - Ob Estuary, 30 μm (St. 10, 0 m);

c - the most common form in all samples, Yenisei Estuary, 10 μm (St.30, 12 m);

d - Ob Estuary, 6 μm (St. 48, 7 m);

parts of the estuaries. In the studied particles the gold exists in different mineral forms in different associations with other chemical elements (Fig. 4).

The particles having a small addition of Si are more common (Fig. 4a). We found many particles wich contain Si, Al and Fe together with Au in different relations (Fig. 4b,c). The large particles are found on St. 10 where Au exists in combination with Cu, while concentrations of Si, Al and Fe are insignificant.

Thus, analysis of the samples under the electronic microscope and EDAX analyses revealed that in the mixing zone in both estuaries from south to north the character of the suspended particulate matter changes. Comparatively large terrigenous crystallized particles prevail in the river water with salinity less than 4 $^{o}/_{oo}$. In the Kara Sea such particles are rare. There, biogenic particles are more abundant as well as weakly crystallized amorphous alumosilicates and oxyhydroxides of iron and manganese.

Granulometric characteristics of suspended matter

The suspended matter in both estuaries has a pelitic grain size (<10 µm). Variations in grain sizes are small along the transects from the estuaries to the sea (Table 1), although slight difference are noted under the electron microscope. Comparison of the granulometric composition of the suspended particuate matter with aerosols sampled over the Kara Sea during our expedition and previous cruises (Shevchenko et al., in press) showed that the aerosols are coarser than suspended matter.

The dominance of particles with sizes less than 2 µm means that suspended particles have a large sorption surface and allows active removing of chemical elements from estuarian water.

Table 1. Grain-size characteristics of particulate matter

Characteristics	Ob Section			Yenisei Section			Aerosols
Stations	12	17	52	32	27	21	Kara Sea
Average size (µm)	1.43	1.28	1.18	1.29	1.24	1.10	1.53
Median size (µm)	1.05	0.96	0.92	0.97	0.98	0.89	1.13
Particles (%) <2 µm	80	85	90	85	90	95	80
2-5 µm	17	14	9	12	9	4	16
>5 µm	3	1	<1	3	<1	<1	4

Concentration of suspended matter

Concentrations of suspended matter in the Ob Estuary varies from 0.64 mg/l to 15.3 mg/l (Appendix 1). Highest values are observed at the southernmost station (St. 12) ranging from 6.23 mg/l at the surface to 15.3 mg/l in 12 m water depth (1 m above the bottom). The lowest values (0.64 mg/l) are measured in samples, collected over the pycnocline at the northernmost station of the transect (St. 52).

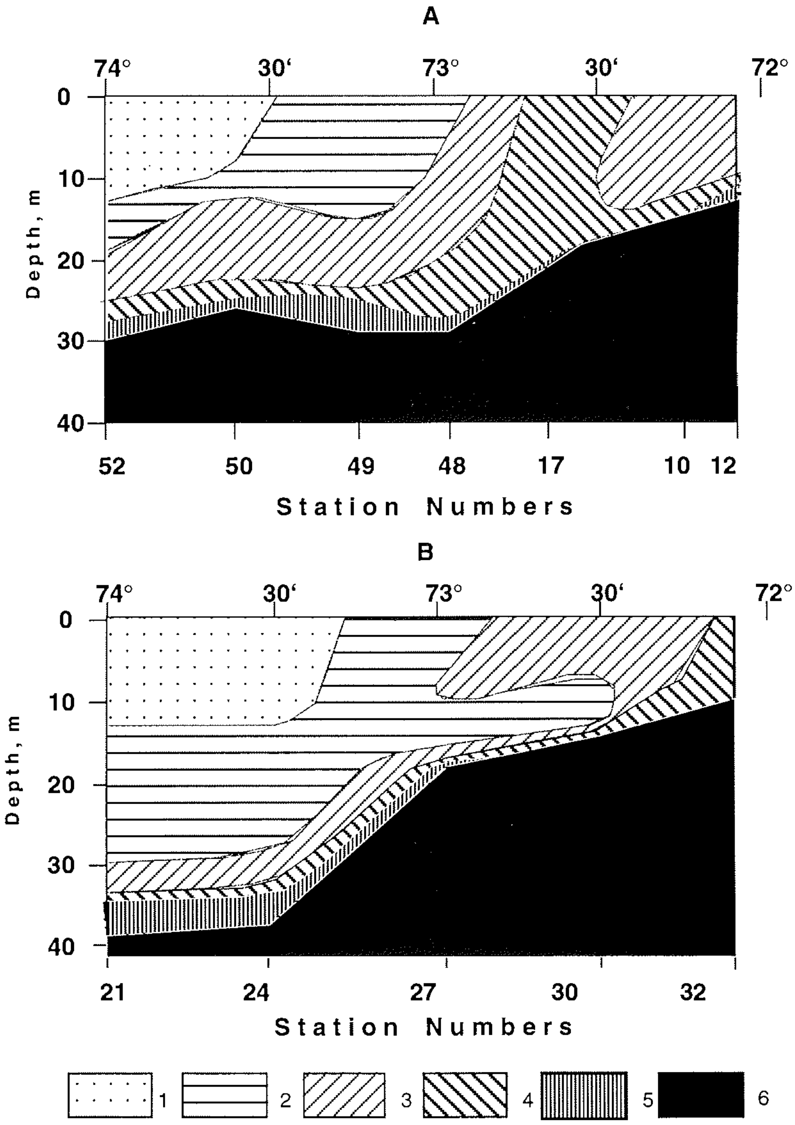


Fig. 5. Distribution of suspended matter (mg/l) on transects in the Ob (a) and Yenisei (b) Estuaries
a: 1 - <1, 2 - 1-2, 3 - 2-5, 4 - 5-10, 5 - >10, 6 - bottom;
b: 1 - <1.5, 2 - 1.5-3, 3 - 3-4.5, 4 - 4.5-6, 5 - >6, 6 - bottom.

Concentrations of suspended matter decrease northward from the fresh river water to sea water (Fig. 5A). High concentrations in comparison with the surrounding water are observed in the mixing zone in the salinity range of 5-10 $^{0}/_{00}$ (St. 17, 48; Table 1, Fig. 5). This increase is related to the coagulation of colloids and fine particles of organic matter, formation of amorphous alumosilicate particles, and precipitation of oxyhydroxide iron and manganese. Maximum quantities of spherical aggregates are found in this zone. Chemical processes cause an enrichment of suspended matter because microelements are removed from the solution due to coprecipitation and adsorption. Further north the suspended matter concentrations decreased to minimal values above the pycnocline layer. Below the pycnocline suspended matter concentrations are slightly higher and highest concentrations are observed near the bottom which may be caused by resuspension of sediments by near-bottom currents and formation of a nepheloid layer.

Along the transect in the Yenisei estuary the same situation is observed. Concentrations of suspended matter vary from 1.04 to 11 mg/l. Minimum values are found above the pycnocline layer at the sea's end of the transect, and the maximum in the near-bottom layer with resuspended material. Concentrations of the suspended matter in this Estuary are approximately twice lower than in the Ob Estuary under comparable salinity conditions. The pattern of suspended matter distribution is similar to the Ob Estuary. Concentrations decrease from the south to the north (Fig. 5b). In the salinity range from 4 to 8 $^{0}/_{00}$ concentrations of suspended matter increase which is related to coagulation of colloids. Very high concentrations as in the Ob Estuary are observed there.

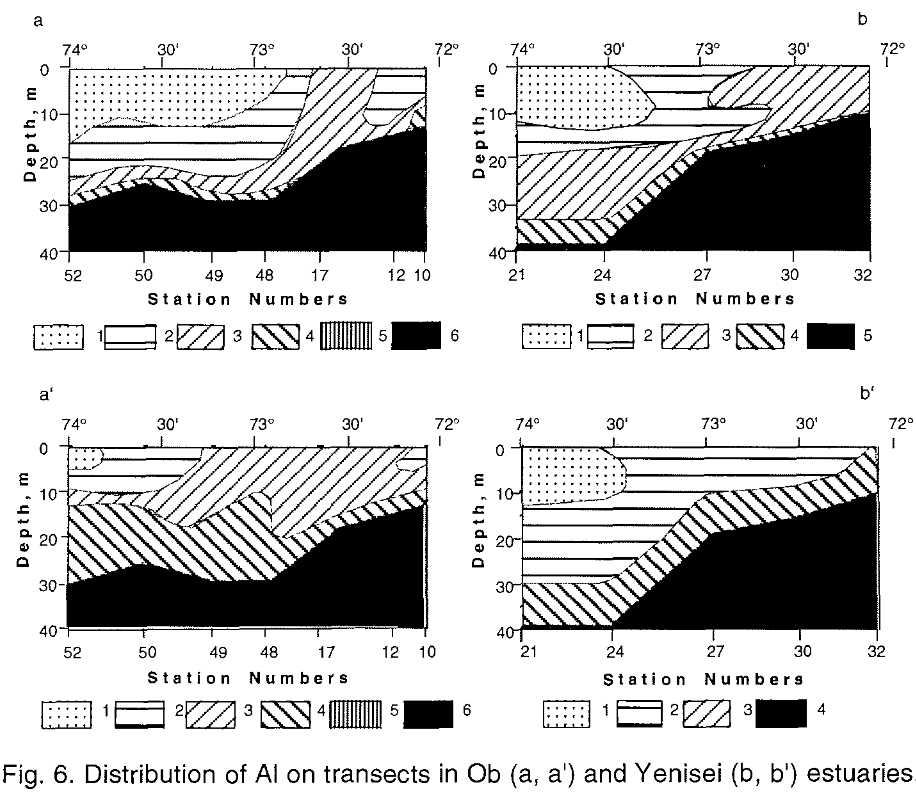


Fig. 6. Distribution of Al on transects in Ob (a, a') and Yenisei (b, b') estuaries.
a, µg/l : 1 - <100, 2 - 100-200, 3 - 200-400, 4 - 400-800, 5 - >800, 6 - bottom;
a', %: 1 - <3, 2 - 3-5, 3 - 5-7, 4 - >7, 5 - bottom;
b, µg/l: 1 - <100, 2 - 100-200, 3 -200-500, 4 >500, 5 - bottom;
b', %: 1 - <5, 2 - 5-7, 3 - >7.

Thus, the distribution of suspended matter in both estuaries is similar, although concentration values are different. This depends on different conditions in the watershed basins. The Ob River and its tributaries flow through the western Siberian Lowlands, where unconsolidated sediments are exposed, while Yenisei River crosses mountainous regions with prevailing crystalline rocks, mainly Siberian trap basalts (Koronovsky, 1984; Lightfoot et al., 1990). Comparison of our data with data of the 49 cruise of RV "Dmitry Mendeleev" in 1993 (Shevchenko et al., 1996, 1997) shows that concentrations of suspended matter and their distributions are very similar in September 1993 and 1997.

Distribution of chemical elements

The suspended matter consists of terrigenous material (Al, Si, Ca and Fe are indicator elements), and biogenic matter which consists of particulate organic carbon, amorphous silica and phosphorus which can be in organic or mineral forms. Moreover, during mixing of fresh river water and sea water a variety of minerals (for example, oxyhydroxides of iron and manganese) and organic sorbents are formed. During formation they coprecipitate and adsorb a large range of microelements including heavy metals.

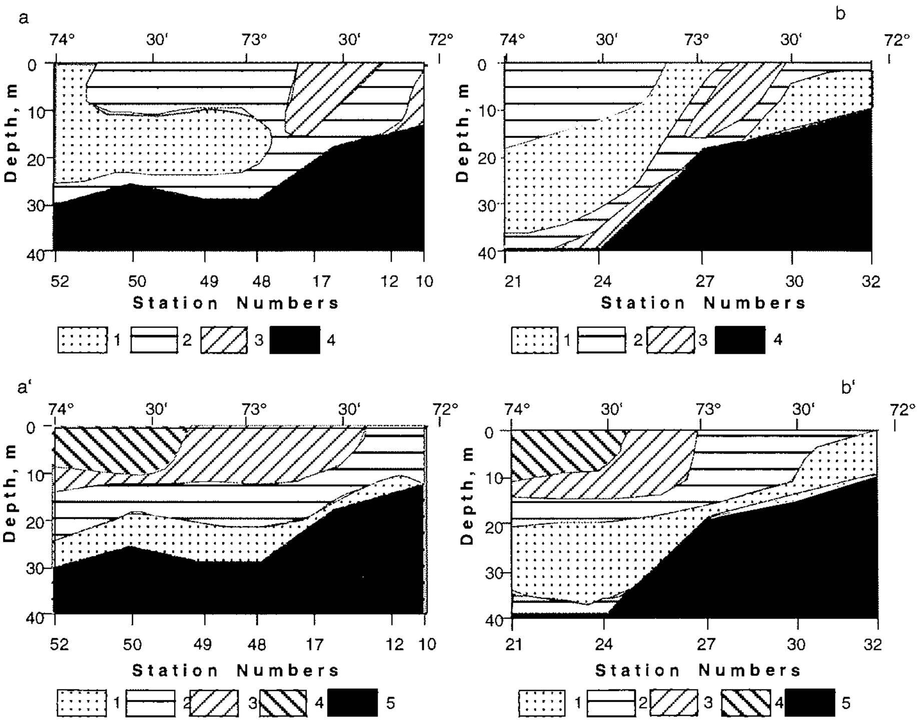


Fig. 7. Distribution of particulate organic carbon on transects in Ob (a, a') and Yenisei (b, b') estuaries.

a (μg/l): 1 - <200, 2 - 200-500, 3 - >500, 4 - bottom;

a', b' (%): 1 - <5, 2 - 5-10, 3 - 10-20, 4 - >20, 5 - bottom;

b (μg/l): 1 - <200, 2 - 200-300, 3 - >300, 4 - bottom;

The distribution of aluminium in the estuaries of the Ob and Yenisei rivers is similar to the concentrations of the suspended matter (Fig. 6). This is easily explained by the fact that the main part of the suspended matter consists of particles of terrigenous origin and the decrease of concentrations is controlled first of all by sedimentation of mineral particles. The zone of high concentrations of Al is also observed in the salinity range of 5-10 $^{o}/_{oo}$ where coagulation of colloidal matter and transfer lead to the formation of suspended matter. Further offshore both concentrations and percentage abundance of Al in the suspended matter decrease (Fig. 6a, b). This is caused by dilution of terrigenous components with flocculating organic matter, because of a decrease of terrigenous components in the distal areas of the estuaries on the one hand, on the other hand because organic matter is enriched constantly as a result of production above the pycnocline layer (primary production). In the zone of colloid coagulation the increase of Al contents in the suspended matter is not observed due to a high degree of coagulation of organic matter and oxyhydroxides of iron diluting the Al contents.

Particulate organic carbon (POC) shows a tongue with peak concentrations in both estuaries in the zone of extensive mixing. In the Ob Estuary concentrations are low at both ends of the transect increasing to the zone of intensive mixing (S= 5-10 $^{o}/_{oo}$) (Fig. 7a). POC concentrations are low under the pycnocline layer from the mixing zone to the open sea. They are again high near the bottom along the transect. In the Yenisei Estuary distribution of POC is similar except for a decrease in a wide band from the surface to the deeper waters below the pycnocline north of the intensive mixing zone (Fig. 7b).

Although POC has a similar distribution pattern in both estuaries differences in POC concentrations are the result of different character of supply from the rivers. The Ob River transports organic rich matter from e.g. peat bogs located in the catchment area, while the Yenisei River flows through mountaineous areas with basic igneous rocks transporting low amounts of organic matter to the estuary. This is well illustrated by Figures 7a´ and 6b´ showing that the POC contents in the suspended matter in the Ob river exceed these of the Yenisei River by a factor of two. The character of the POC distribution in the suspended matter is similar in both estuaries: the contents of POC increase from south to north and become similar, probably because of an overall increase in photosynthetic production of organic matter and/or a decrease in minerogenic particles in the suspended matter. This is confirmed by investigations on biomarkers from water samples collected in September 1993 (Aleksandrova and Shevchenko, 1997).

The concentration increase in the intensive mixing zone is related to coagulation of organic colloids and formation of suspended particles. Dai and Martin (1995) studied the behaviour of some chemical elements in the Ob and Yenisei estuaries in September 1993. They showed that contents of organic colloids sharply decreased in the zone of salinity increase from 5 to 10 $^{o}/_{oo}$. At higher salinities contents decreased remaining low until the end of the transects in both estuaries.

Iron is present in the suspended matter as Fe-alumosilicates and oxyhydroxides. The distribution of iron like that of aluminium is controlled first of all by concentrations of the suspended matter. Distribution of Fe contents in the suspended matter of both estuaries are almost similar. They are maximum in the zone of intensive mixing and decrease over the pycnocline seaward (Fig. 8a, b). Iron concentrations are more than two times higher in the Ob Estuary than in the Yenisei Estuary in the zone of intensive mixing. This is due to both higher suspended matter concentrations and higher contents of iron in the particulate material.

There is an essential difference in the southern areas of estuaries. In the Ob Estuary the zone of high concentrations begins just at the southern end of the transect (St. 12) whereas in the Yenisei Estuary this zone begins further north at St. 30. Intensive coagulation of Fe-colloids begins at salinities around 2 $^{o}/_{oo}$ (Sholkovitz, 1976). In the Ob Estuary salinity is already higher at the southern end of the transect and the zone of intensive transformation of colloids to suspension begins south of this point. In the Yenisei Estuary the salinity at the southern station (St. 32) is less than 2 $^{o}/_{oo}$ (Fig. 2) and intensive coagulation of the colloids does not occur. Dai and Martin (1995) also showed that most intensive decrease of concentrations of colloidal Fe occurred in September 1993 at salinities lower than 5 $^{o}/_{oo}$ both in Ob and Yenisei estuaries.

The zone for Al and C_{org} coagulation is located a little to the north where the salinities are higher (Fig. 6, 7). Fe content in the total suspended matter is maximum in the zone of colloid coagulation and it decrease northward probably due to dissolution triggered by biogenic production over the pycnocline in the estuaries.

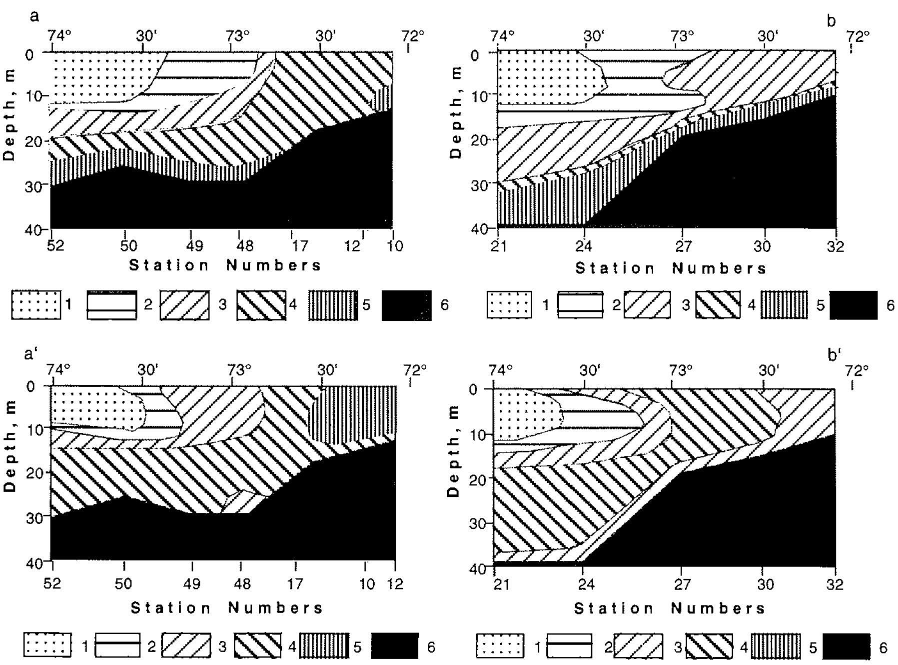


Fig. 8. Distribution of Fe on transects in Ob (a, a') and Yenisei (b, b') estuaries. a, b (μg/l): 1 - <100, 2 - 100-200, 3 - 200-400, 4 - 400-800, 5 - >800, 6 - bottom; a', b' (%): 1 - <5, 2 - 5-7, 3 - 7-9, 4 - 9-11, 5 - >11;

Contents of manganese in the particulate matter increase from the estuaries to the sea (Fig. 9a). Mn contents at the southern end of the Ob transect are lower than 0.1% and correspond to contents of Mn in the soils and the sedimentary rocks of the river basin. In the zone of coagulation of Fe-colloids the Mn ions are adsorbed on them resulting in an increase of manganese content in the particulate matter. The significant decrease around St. 17 is likely related to the desorption of Mn and dilution by coagulating organic matter and alumosilicates. Then contents increase especially strongly in the upper part of the pycnocline and the surface water layer. Mn contents here are higher by one order of magnitude than in the southern part of the transect. Mn is likely oxidized because of microbial activity and transformation to oxyhydroxides, which is a good sorbent for many trace elements.

The distribution of manganese along the Yenisei is similar to the Ob Estuary. Contents of Mn increase northward because of formation of oxyhydroxides, in particular above the pycnocline layer. The zone of desorption (minimum Mn contents) likely exists in the Yenisei Estuary but our data do not show it because we have sampled too few stations. This zone is probably located between stations 27 and 30.

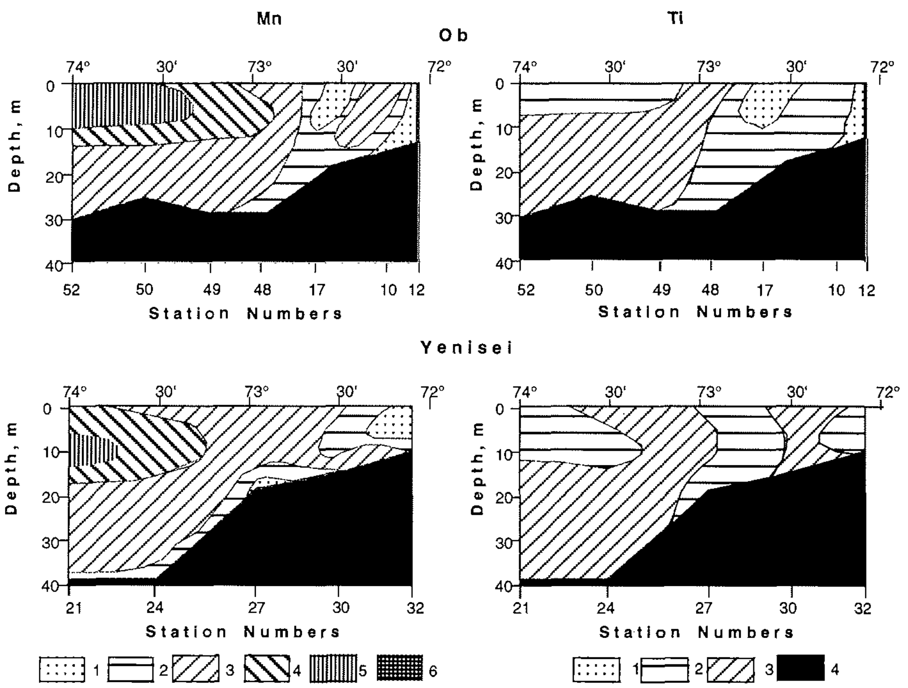


Fig. 9. Distribution of Mn and Ti in suspended matter on transects in Ob (a, a') and Yenisei (b, b') Estuaries (%).
Mn : 1 - <0.1, 2 - 0.1-0.2; 3 - 0.2-0.5; 4 - 0.5-1; 5 - >1; 6 - bottom;
Ti: 1 - <0.2; 2 - 0.2-0.4; 3 - >0.4; 4 - bottom.

Titanium is enriched by a factor of two in suspended matter of the Yenisei Estuary compared to the Ob Estuary because the Yenisei River and its tributaries flow through Siberian trap basalts which contain more than 1% Ti (Lightfoot et al., 1990), while the Ob River crosses peat bogs in lowlands with low concentrations of Ti. Despite of differences in contents in the suspended matter in the southern parts of the transects the distributions in both estuaries is similar. In the southern parts of the transects Ti contents are minimal and at the southern end of the zone of river and seawater mixing (S = 2-5 $^{o}/_{oo}$) they increase by 1.5 times. Then contents decrease again at salinities of more than 5 $^{o}/_{oo}$ in the zone of Al and organic matter coagulation, and then they increase again.

It should be noted that titanium is considered as one of the most inert elements in the earth´s rocks because its contents in the crust and in the soils are practically not different. Ti is concentrated in minerals resistent towards weathering (anatase, rutile, sphene, and others) and remains in the weathering crust. Low amounts of Ti are found in dark-colored femic minerals (amphiboles, pyroxenes, hornblendes, micas) which can be mobilized during weathering under certain physicochemical conditions. It may form organic and inorganic complexes and oxyhydroxides (dissolved and colloidal forms) and may also contribute to the composition of clay minerals. Ti can be transported in this forms over long distances and may accumulate in pelagic sediments where around 60% of Ti is found in hydrogenic form (Lisitsyn et al., 1980). In the zone of fresh and saline water mixing the colloids containing titanium coagulate increasing its content in suspended matter. With increasing salinity to 5 $^{o}/_{oo}$ the most intensive coagulation of organic and alumosilicate colloids occurs leading to dilution of the titanium contents. After the process of intensive coagulation ended, the Ti contents increase again and obtains constant concentrations in seawater under the pycnocline layer. Above this layer in the sea part of transects Ti decrease because of the dilution by organic matter production.

Relatively high numbers of Ti-rich particles in suspended matter in the outer part of Yenisei Estuary in September 1993 has been found also by electron probe x-ray microanalysis (Jambers et al., 1997).

The chemical behaviour of Si and Ca is similar to that of Al, because these elements occur together in fine terrigenous minerals. Phosphorus and amorphous silica is likely incorporated in the biogenic components of the suspended matter, although P was found together with Al, Si and Ca in particles studied by EDAX.

Results of factor analysis

As a rule the microelements do not form independent mineral phases but they exist in isomorphic relations with major elements in terrigenous minerals or are adsorbed on colloidal coagulating particles. A factor analysis was carried out on the chemical composition of suspended particulate material (for both rivers) to find relationships between elements and distribution patterns. Five main factors explain 73.7% of the variance in the composition (Fig. 10). The first factor (with a variance of 33.3%) reflects the impact of fine-dispersed and clay materials: the factor is mainly determined by Si, Al, Fe, Ti, Ca and several other microelements. The second factor (18.8% variance) charac-terizes the influence of coagulating and flocculating matter formed in the estuaries which adsorbe microelements. The factor is determined by Mn, Ti, Co, Cr, V, Ni, As, Pb, POC and Ba. The third factor has a variance of 19.9%. It is charcterized by biogenic elements (Si_{am}, P, POC), salinity and elements associated with biogenic matter (Sr, Pb, As, Zn, Ba, Fe). The fourth factor (variance 6.1%) is characterized by the influence of finely dispersed possibly Fe-oxyhydroxides and probably Fe-siliceous compounds, which bind P, Zn, Co, Ni, Ti, V and Ba. The fifth factor (4.6% variance) shows a positive correlation of salinity, POC and Ba, which is likely to reflect the increase of organic matter by primary production and adsorbed microelements.

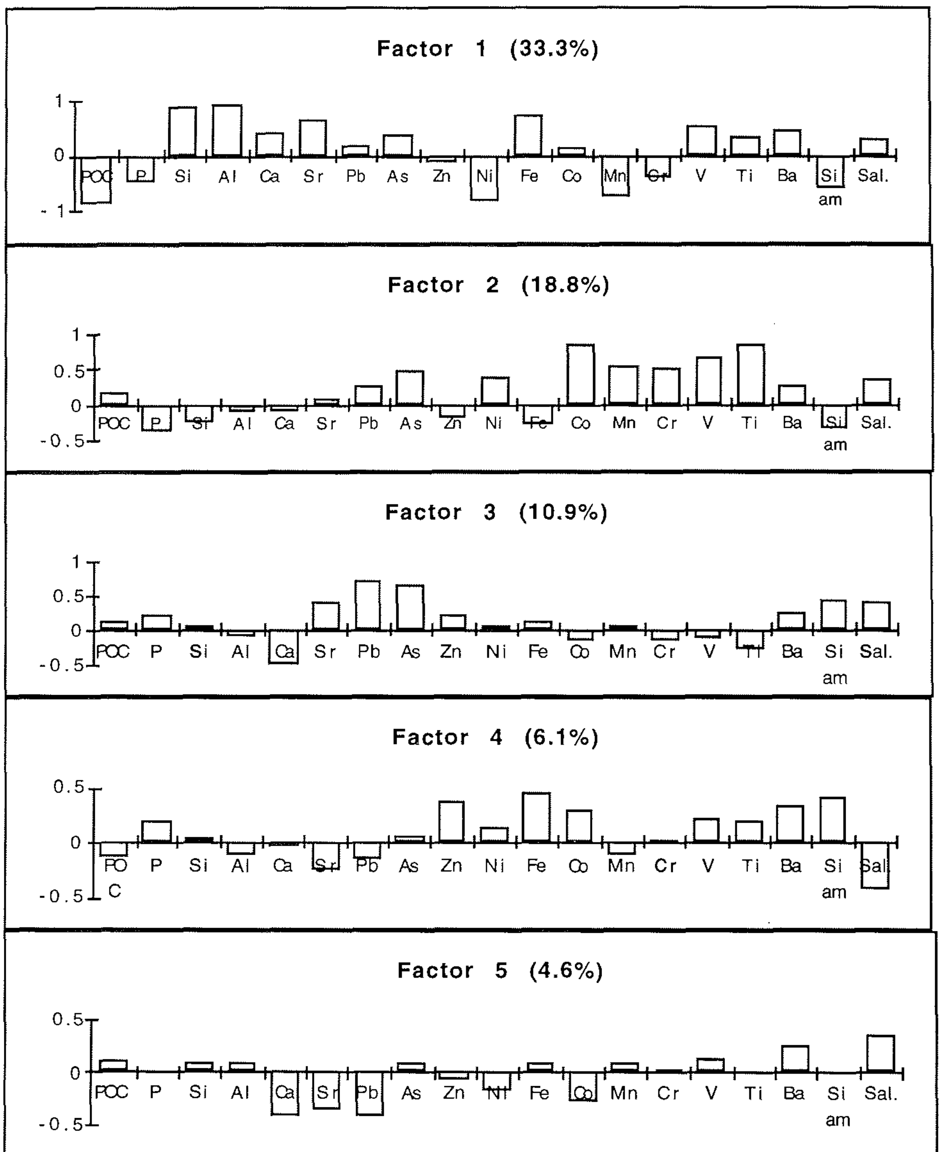


Fig. 10. Results of factor analysis.

Conclusions

Our data show the presence of a mixing zone along the whole transects in both estuaries. Processes of suspended matter transformation occur along the total length of the estuaries. Firstly, the coarse grains settle down in the southernmost part, where flow rates decrease because of the widening of the river mouths. This process leads to the transformation of coarse to fine suspensions. Then coagulation of the colloids occurs at salinities from 2 to 10 $^{o}/_{oo}$. There colloidal aggregates and other fine particles (for example, clay minerals) precipitate, and adsorb and coprecipitate a large range of chemical elements. During this process the formation of suspended matter takes place. Newly formed suspended matter differs from riverine material. As a result the suspended matter is enriched with certain elements. The marine primary production of organic matter is incorporated in the suspended matter, transformating it to marine particulate material.

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Appendix 1: Location of the sampling stations and horizons, data on particulate material concentrations and concentrations and contents of chemical elements.

Station No.	Latitude N	Longitude E	Water Depth (m)	Sample Depth (m)	Suspension Concentration mg/l	POC (µg/l)	POC (%)	P (µg/l)	P (%)	Si (µg/l)	Si (%)	Al (µg/l)	Al (%)	Ca (µg/l)	Ca (%)	Sr (µg/l)	Sr (%)	Pb µg/l	Pb (%)	As µg/l	As (%)
Ob Transect																					
12	72°10.31´	74°17.37´	13.0	0.0	6.23	590.0	9.5	12.460	0.20	1351.91	21.7	292.81	4.70	17.444	0.28	1.0217	0.0164	0.1744	0.0028	0.12460	0.0020
				8.0	7.51	691.0	9.2	24.783	0.33	1900.03	25.3	458.11	6.10	36.799	0.49	1.6071	0.0214	0.3079	0.0041	0.09763	0.0013
				12.0	15.3	3160.0	20.6	27.540	0.18	4253.40	27.8	1231.65	8.05	13.158	0.09	2.9529	0.0193	0.4284	0.0028	0.06120	0.0004
10	72°30.02´	74°04.86´	15.0	0.0	4.62	404.0	8.7	17.556	0.38	1131.90	24.5	286.44	6.20	8.778	0.19	0.5775	0.0125	0.1987	0.0043	0.13398	0.0029
				10.0	4.02	362.0	9.0	10.050	0.25	940.68	23.4	233.16	5.80	8.442	0.21	0.5829	0.0145	0.2010	0.0050	0.09648	0.0024
				11.5	7.58	379.0	5.0	23.498	0.31	2092.08	27.6	545.76	7.20	12.128	0.16	1.3568	0.0179	0.3108	0.0041	0.14402	0.0019
				13.0	6.45	259.0	4.0	22.575	0.35	2076.90	32.2	574.05	8.90	15.480	0.24	1.5545	0.0241	0.3225	0.0050	0.11610	0.0018
17	72°41.32´	73°43.84´	21.0	0.0	7.36	893.0	12.1	15.456	0.21	1825.28	24.8	471.00	6.40	25.024	0.34	1.8621	0.0253	0.3018	0.0041	0.17664	0.0024
				5.5	5.40	562.0	10.4	14.040	0.26	1366.20	25.3	340.20	6.30	15.120	0.280	1.6200	0.0300	0.3834	0.0071	0.14580	0.0027
				9.0	7.61	809.0	10.6	13.698	0.18	1811.18	23.8	471.82	6.20	21.308	0.28	2.3363	0.0307	0.4186	0.0055	0.21308	0.0028
				18.0	5.62	354.0	6.3	11.802	0.21	1500.54	26.7	415.88	7.40	29.224	0.52	1.9277	0.0343	0.4946	0.0088	0.25290	0.0045
48	72°57.68´	73 08.86	29.0	0.0	1.43	228.0	15.9	1.859	0.13	308.88	21.6	81.51	5.70	1.001	0.07	0.2717	0.0190	0.0644	0.0045	0.04004	0.0028
				7.0	2.33	242.0	10.4	4.660	0.20	519.59	22.3	137.47	5.90	6.757	0.29	0.6011	0.0258	0.1235	0.0053	0.04194	0.0018
				11.0	3.74	202.0	5.4	6.732	0.18	994.84	26.6	291.72	7.80	15.708	0.42	1.0659	0.0285	0.2020	0.0054	0.10098	0.0027
				24.0	5.04	248.0	4.9	6.048	0.12	1325.52	26.3	378.00	7.50	9.072	0.18	1.2751	0.0253	0.1109	0.0022	0.14112	0.0028
49	73°12.64´	72°54.11´	29.0	0.0	2.00	330.0	16.5	5.000	0.25	460.00	23.0	108.00	5.40	5.000	0.25	0.6660	0.0333	0.1600	0.0080	0.06200	0.0031
				11.0	1.53	176.0	11.5	2.448	0.16	379.44	24.8	100.98	6.60	4.590	0.30	0.4544	0.0297	0.1163	0.0076	0.06732	0.0044
				16.0	2.34	173.0	7.4	4.446	0.19	585.00	25.0	166.14	7.10	5.850	0.25	0.7699	0.0329	0.1778	0.0076	0.08190	0.0035
				27.0	13.07	379.0	2.9	18.298	0.14	3698.81	28.3	1032.53	7.90	53.587	0.41	3.9471	0.0302	0.7450	0.0057	0.56201	0.0043
50	73°36.40´	72°57.50´	26.0	0.0	0.84	219.0	26.0	2.268	0.27	132.72	15.8	30.24	3.60	1.764	0.21	0.0395	0.0047	0.0244	0.0029	0.00168	0.0002
				9.0	1.08	256.0	23.7	2.160	0.20	189.00	17.5	44.28	4.10	1.620	0.15	0.2063	0.0191	0.0616	0.0057	0.03132	0.0029
				13.0	2.34	150.0	6.4	5.382	0.23	608.40	26.0	166.14	7.10	6.318	0.27	0.8728	0.0373	0.2551	0.0109	0.14274	0.0061
				20.0	4.58	154.0	3.4	5.954	0.13	1190.80	26.0	338.92	7.40	15.572	0.34	1.3877	0.0303	0.3481	0.0076	0.25190	0.0055
52	74°00.0´	72°39.7´	30.0	0.0	0.64	185.0	29.1	1.856	0.29	84.48	13.2	18.56	2.90	0.448	0.07	0.1037	0.0162	0.0352	0.0055	0.00640	0.0010
				7.0	0.64	196.0	30.4	1.472	0.23	98.56	15.4	22.40	3.50	0.704	0.11	0.1485	0.0232	0.0371	0.0058	0.02176	0.0034
				10.0	0.92	105.0	11.4	1.380	0.15	217.12	23.6	57.04	6.20	0.736	0.08	0.1822	0.0198	0.0524	0.0057	0.02760	0.0030
				27.0	9.3	360.0	3.9	17.670	0.19	2585.40	27.8	734.70	7.90	42.780	0.46	2.6877	0.0289	0.2418	0.0026	0.39990	0.0043

Appendix 1 cont´d: Location of the sampling stations and horizons, data on particulate material concentrations and concentrations and contents of chemical elements.

Station No.	Latitude N	Longitude E	Water Depth (m)	Sample Depth (m)	Suspension Concentration mg/l	POC (µg/l)	POC (%)	P (µg/l)	P (%)	Si (µg/l)	Si (%)	Al (µg/l)	Al (%)	Ca (µg/l)	Ca (%)	Sr (µg/l)	Sr (%)	Pb µg/l	Pb (%)	As µg/l	As (%)
Yenisei Transect																					
32	72°05.53´	81°28.50´	10.0	0.0	4.42	248.0	5.6	10.166	0.23	1193.40	27.0	327.08	7.40	50.388	1.14	1.2420	0.0281	0.1680	0.0038	0.00442	0.0001
				5.0	4.67	191.0	4.1	9.340	0.20	1144.15	24.5	308.22	6.60	36.426	0.78	1.4991	0.0321	0.2942	0.0063	0.07472	0.0016
				8.0	4.74	157.0	3.3	8.058	0.17	1175.52	24.8	322.32	6.80	40.764	0.86	1.2988	0.0274	0.1896	0.0040	0.06162	0.0013
30	72°30.51´	80°20.10´	15.0	0.0	3.57	221.0	6.2	6.069	0.17	813.96	22.8	232.05	6.50	30.702	0.86	0.5855	0.0164	0.0214	0.0006	0.01071	0.0003
				5.0	3.84	122.0	3.2	5.760	0.15	860.16	22.4	249.60	6.50	16.896	0.44	1.1290	0.0294	0.1958	0.0051	0.06144	0.0016
				10.0	2.66	187.0	7.0	4.522	0.17	649.04	24.4	194.18	7.30	15.162	0.57	0.5746	0.0216	0.0825	0.0031	0.03724	0.0014
				12.0	2.5			3.500	0.14	577.50	23.1	165.00	6.60	14.250	0.57	0.5700	0.0228	0.1050	0.0042	0.04250	0.0017
27	72°53.21´	80°05.33´	19.0	0.0	1.89	146.0	7.7	3.024	0.16	430.92	22.8	120.96	6.40	13.608	0.72	0.4876	0.0258	0.1210	0.0064	0.04347	0.0023
				8.0	3.78	378.0	10.0	6.426	0.17	907.20	24.0	257.04	6.80	15.498	0.41	0.2495	0.0066	0.0000		0.06048	0.0016
				14.0	2.2			3.080	0.14	534.60	24.3	154.00	7.00	10.120	0.46	0.6710	0.0305	0.1232	0.0056	0.03740	0.0017
				18.0	11.04	265.0	2.4	17.664	0.16	3135.36	28.4	938.40	8.50	112.608	1.02	3.1795	0.0288	0.6072	0.0055	0.17664	0.0016
24	73°32.07´	79°55.27´	40.0	0.0	1.5	294.0	19.6	2.550	0.17	349.50	23.3	100.00	6.70	6.600	0.44	0.3300	0.0222	0.0800	0.0054	0.06000	0.0040
				12.0	1.04	183.0	17.6	2.392	0.23	208.00	20.0	52.00	5.00	1.976	0.19	0.1799	0.0173	0.0582	0.0056	0.02080	0.0020
				20.0	3.58	176.0	4.9	7.160	0.20	869.94	24.3	250.60	7.00	16.468	0.46	0.9594	0.0268	0.1575	0.0044	0.08234	0.0023
				35.0	9.23	397.0	4.3	10.153	0.11	2335.19	25.3	673.79	7.30	40.612	0.44	2.5106	0.0272	0.4523	0.0049	0.29536	0.0032
39	73°32.16´	79°55.05´	31.5	0.0	1.06	276.0	26.1	1.908	0.18	159.00	15.0	32.86	3.10	0.742	0.07	0.1155	0.0109	0.0445	0.0042	0.00000	
				11.0	1.08	310.0	28.6	1.620	0.15	184.68	17.1	39.96	3.70	0.756	0.07	0.2398	0.0222	0.0810	0.0075	0.01188	0.0011
				20.0	2.17	204.0	9.4	3.038	0.14	505.61	23.3	141.05	6.50	11.718	0.54	0.6640	0.0306	0.1215	0.0056	0.04123	0.0019
				28.0	2.22	208.0	9.4	2.886	0.13	519.48	23.4	148.74	6.70	18.204	0.82	0.6549	0.0295	0.1221	0.0055	0.05550	0.0025
21	74° 02.40´	81°00.27´	40.0	0.0	1.24	265.0	21.4	3.720	0.30	233.12	18.8	53.32	4.30	2.728	0.22	0.2790	0.0225	0.0756	0.0061	0.01984	0.0016
				10.0	1.13	263.0	23.2	3.729	0.33	201.14	17.8	42.94	3.80	4.407	0.39	0.0000		0.0136	0.0012	0.01469	0.0013
				15.0	2.8	221.0	7.9	3.640	0.13	658.00	23.5	190.40	6.80	12.040	0.43	0.7028	0.0251	0.1204	0.0043	0.08120	0.0029
				35.0	10.47	178.0	1.7	11.517	0.11	2701.26	25.8	816.66	7.80	90.042	0.86	2.2406	0.0214	0.4397	0.0042	0.32457	0.0031

Appendix 1 cont´d: Location of the sampling stations and horizons, data on particulate material concentrations and concentrations and contents of chemical elements.

Station No.	Zn µg/l	Zn (%)	Ni µg/l	Ni (%)	Fe µg/l	Fe (%)	Co µg/l	Co (%)	Mn µg/l	Mn (%)	Cr µg/l	Cr (%)	V µg/l	V (%)	Ti µg/l	Ti (%)	Ba µg/l	Ba (%)	Siam µg/l	Siam (%)
12	10.3916	0.1668	0.86597	0.0139	697.76	11.2	0.06853	0.0011	3.115	0.05	0.41741	0.0067	0.97188	0.0156	9.345	0.15	6.230	0.10	414.918	6.66
	15.5757	0.2074	1.38935	0.0185	923.73	12.3	0.12767	0.0017	3.004	0.04	0.54823	0.0073	1.21662	0.0162	12.016	0.16	7.510	0.10	434.078	5.78
	3.2895	0.0215	1.43820	0.0094	1331.10	8.7	0.12240	0.0008	1.530	0.01	1.07100	0.0070	2.43270	0.0159	32.130	0.21	13.770	0.09	312.120	2.04
10	2.2176	0.0480	0.77616	0.0168	563.64	12.2	0.10626	0.0023	9.240	0.20	0.41118	0.0089	0.83160	0.0180	12.012	0.26	5.082	0.11	215.292	4.66
	2.1708	0.0540	0.81204	0.0202	442.20	11.0	0.06834	0.0017	11.658	0.29	0.28944	0.0072	0.58692	0.0146	10.050	0.25	4.422	0.11	194.568	4.84
	4.0932	0.0540	1.25070	0.0165	848.96	11.2	0.16676	0.0022	10.612	0.14	0.83380	0.0110	1.32650	0.0175	22.740	0.30	7.580	0.10	345.648	4.56
	1.5480	0.0240	0.54180	0.0084	580.50	9.0	0.07095	0.0011	0.645	0.01	0.47730	0.0074	1.03200	0.0160	12.900	0.20	6.450	0.10	239.940	3.72
17	3.6947	0.0502	0.66240	0.0090	743.36	10.1	0.08096	0.0011	0.736	0.01	0.49312	0.0067	1.17760	0.0160	12.512	0.17	7.360	0.10	318.080	4.32
	3.6450	0.0675	0.6534	0.01210	491.40	9.1	0.06480	0.0012	0.540	0.01	0.37800	0.0070	0.82080	0.0152	7.5600	0.14	4.860	0.09	277.560	5.14
	4.1703	0.0548	0.74578	0.0098	844.71	11.1	0.17503	0.0023	10.654	0.14	0.60880	0.0080	1.23282	0.0162	19.025	0.25	8.371	0.11	301.356	3.96
	11.5603	0.2057	0.95540	0.0170	578.86	10.3	0.17422	0.0031	8.992	0.16	0.56762	0.0101	0.94416	0.0168	16.298	0.29	5.620	0.10	169.724	3.02
48	0.7779	0.0544	0.28028	0.0196	125.84	8.8	0.04433	0.0031	6.864	0.48	0.27170	0.0190	0.26026	0.0182	7.579	0.53	1.716	0.12	48.048	3.36
	0.8178	0.0351	0.51726	0.0222	200.38	8.6	0.05825	0.0025	13.747	0.59	0.31455	0.0135	0.34717	0.0149	7.223	0.31	2.097	0.09	79.686	3.42
	1.3614	0.0364	0.66572	0.0178	392.70	10.5	0.08976	0.0024	10.846	0.29	0.40392	0.0108	0.61710	0.0165	14.212	0.38	3.740	0.10	61.336	1.64
	2.7216	0.0540	0.40824	0.0081	438.48	8.7	0.08064	0.0016	8.064	0.16	0.53928	0.0107	1.00800	0.0200	16.632	0.33	4.536	0.09	115.920	2.30
49	0.8040	0.0402	0.42600	0.0213	166.00	8.3	0.06400	0.0032	17.400	0.87	0.25200	0.0126	0.34000	0.0170	7.200	0.36	1.800	0.09	114.400	5.72
	0.5707	0.0373	0.28611	0.0187	153.00	10.0	0.05661	0.0037	9.333	0.61	0.26622	0.0174	0.32895	0.0215	9.180	0.60	1.683	0.11	56.304	3.68
	0.9337	0.0399	0.39312	0.0168	234.00	10.0	0.07956	0.0034	8.892	0.38	0.28314	0.0121	0.48204	0.0206	11.466	0.49	2.574	0.11	53.352	2.28
	4.6660	0.0357	1.62068	0.0124	1463.84	11.2	0.45745	0.0035	48.359	0.37	1.58147	0.0121	2.87540	0.0220	62.736	0.48	14.377	0.11	394.714	3.02
50	0.5888	0.0701	0.27888	0.0332	43.68	5.2	0.01848	0.0022	11.508	1.37	0.45024	0.0536	0.13440	0.0160	1.932	0.23	0.504	0.06	35.952	4.28
	0.5033	0.0466	0.37800	0.0350	42.12	3.9	0.03456	0.0032	16.200	1.50	0.17172	0.0159	0.17820	0.0165	3.996	0.37	0.864	0.08	47.304	4.38
	1.7644	0.0754	0.55926	0.0239	215.28	9.2	0.11232	0.0048	17.082	0.73	0.55926	0.0239	0.53586	0.0229	13.104	0.56	2.574	0.11	76.752	3.28
	1.0992	0.0240	0.32060	0.0070	444.26	9.7	0.10992	0.0024	10.534	0.23	0.45342	0.0099	0.94348	0.0206	17.862	0.39	5.038	0.11	106.256	2.32
52	0.3322	0.0519	0.19840	0.0310	26.24	4.1	0.01408	0.0022	8.128	1.27	0.08000	0.0125	0.09344	0.0146	1.024	0.16	0.512	0.08	25.088	3.92
	0.3354	0.0524	0.16832	0.0263	25.60	4.0	0.02176	0.0034	10.176	1.59	0.13824	0.0216	0.11328	0.0177	2.624	0.41	0.768	0.12	26.880	4.20
	1.0700	0.1163	0.21068	0.0229	75.44	8.2	0.03312	0.0036	5.980	0.65	0.15088	0.0164	0.19688	0.0214	4.600	0.50	1.564	0.17	34.592	3.76
	2.0274	0.0218	1.06950	0.0115	911.40	9.8	0.40920	0.0044	49.290	0.53	1.49730	0.0161	2.39010	0.0257	50.220	0.54	10.230	0.11	234.360	2.52

Appendix 1 cont´d: Location of the sampling stations and horizons, data on particulate material concentrations and concentrations and contents of chemical elements.

Station No.	Zn µg/l	Zn (%)	Ni µg/l	Ni (%)	Fe µg/l	Fe (%)	Co µg/l	Co (%)	Mn µg/l	Mn (%)	Cr µg/l	Cr (%)	V µg/l	V (%)	Ti µg/l	Ti (%)	Ba µg/l	Ba (%)	Siam µg/l	Siam (%)
32	1.7636	0.0399	0.61880	0.0140	375.70	8.5	0.11492	0.0026	3.536	0.08	0.53924	0.0122	0.80886	0.0183	15.912	0.36	3.978	0.09	146.744	3.32
	1.4150	0.0303	0.53705	0.0115	387.61	8.3	0.13543	0.0029	3.269	0.07	0.50436	0.0108	0.80791	0.0173	14.477	0.31	4.203	0.09	157.846	3.38
	2.5833	0.0545	0.76314	0.0161	455.04	9.6	0.13272	0.0028	6.162	0.13	0.48822	0.0103	0.84372	0.0178	17.538	0.37	4.740	0.10	144.096	3.04
30	2.1848	0.0612	0.64260	0.0180	310.59	8.7	0.17493	0.0049	10.353	0.29	0.73542	0.0206	0.68187	0.0191	21.063	0.59	3.570	0.10	71.400	2.00
	2.2003	0.0573	0.59904	0.0156	364.80	9.5	0.12288	0.0032	4.992	0.13	0.42240	0.0110	0.78336	0.0204	16.128	0.42	3.840	0.10	61.440	1.60
	1.0374	0.0390	0.49742	0.0187	250.04	9.4	0.10640	0.0040	9.310	0.35	0.37772	0.0142	0.58254	0.0219	15.428	0.58	2.660	0.10	27.664	1.04
	0.9600	0.0384	0.44500	0.0178	212.50	8.5	0.06750	0.0027	6.000	0.24	0.30000	0.0120	0.45500	0.0182	11.000	0.44	2.250	0.09	49.500	1.98
27	1.5630	0.0827	0.38367	0.0203	185.22	9.8	0.05481	0.0029	3.591	0.19	0.27405	0.0145	0.34965	0.0185	7.182	0.38	1.701	0.09	43.848	2.32
	1.4062	0.0372	0.76734	0.0203	257.04	6.8	0.18144	0.0048	24.948	0.66	0.54432	0.0144	0.77868	0.0206	26.838	0.71	3.402	0.09	84.672	2.24
	1.8238	0.0829	0.28160	0.0128	200.20	9.1	0.05940	0.0027	4.620	0.21	0.37180	0.0169	0.41140	0.0187	7.920	0.36	2.200	0.10	41.800	1.90
	3.3893	0.0307	0.57408	0.0052	850.08	7.7	0.19872	0.0018	7.728	0.07	0.91632	0.0083	1.87680	0.0170	29.808	0.27	11.040	0.10	132.480	1.20
24	0.6300	0.0416	0.25000	0.0164	150.00	10.0	0.06000	0.0041	7.100	0.47	0.34000	0.0228	0.32000	0.0215	9.300	0.62	1.600	0.11	29.500	1.86
	0.5928	0.0570	0.28080	0.0270	60.32	5.8	0.03224	0.0031	7.904	0.76	0.16120	0.0155	0.18200	0.0175	3.952	0.38	0.728	0.07	41.600	4.00
	1.6468	0.0460	0.48330	0.0135	343.68	9.6	0.11098	0.0031	10.024	0.28	0.42960	0.0120	0.75538	0.0211	16.110	0.45	3.580	0.10	68.020	1.90
	3.9689	0.0430	0.79378	0.0086	821.47	8.9	0.29536	0.0032	18.460	0.20	1.13529	0.0123	1.93830	0.0210	41.535	0.45	10.153	0.11	179.062	1.94
39	0.7992	0.0754	0.38796	0.0366	60.42	5.7	0.02120	0.0020	7.526	0.71	0.22366	0.0211	0.14946	0.0141	0.636	0.06	0.530	0.05	53.848	5.08
	0.8024	0.0743	0.34776	0.0322	61.56	5.7	0.02484	0.0023	6.264	0.58	0.10476	0.0097	0.14580	0.0135	0.540	0.05	0.756	0.07	56.808	5.26
	1.2217	0.0563	0.41664	0.0192	197.47	9.1	0.04991	0.0023	4.123	0.19	0.24955	0.0115	0.42098	0.0194	6.510	0.30	1.953	0.09	54.250	2.50
	0.7992	0.0360	0.39072	0.0176	190.92	8.6	0.05772	0.0026	2.886	0.13	0.25752	0.0116	0.44844	0.0202	7.770	0.35	2.220	0.10	43.512	1.96
21	0.4836	0.0390	0.33480	0.0270	43.40	3.5	0.03100	0.0025	7.936	0.64	0.11160	0.0090	0.16988	0.0137	2.604	0.21	0.744	0.06	62.496	5.04
	1.1221	0.0993	0.32205	0.0285	55.37	4.9	0.02712	0.0024	18.193	1.61	0.17515	0.0155	0.20114	0.0178	4.181	0.37	1.017	0.09	63.732	5.64
	1.0444	0.0373	0.47600	0.0170	252.00	9.0	0.05880	0.0021	14.280	0.51	0.38360	0.0137	0.53480	0.0191	14.280	0.51	2.800	0.10	48.720	1.74
	4.4707	0.0427	0.95277	0.0091	963.24	9.2	0.18846	0.0018	35.598	0.34	0.95277	0.0091	1.76943	0.0169	42.927	0.41	10.470	0.10	87.948	0.84

GRAIN-SIZE DISTRIBUTION AND CLAY-MINERAL COMPOSITION IN SURFACE SEDIMENTS AND SUSPENDED MATTER OF THE OB AND YENISEI RIVERS

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Introduction

Numerous investigations of surface sediments showed that clay minerals are valuable tracers for source areas and transport pathways of terrigenous material in the Arctic Ocean (e.g. Stein et al., 1994; Nürnberg et al., 1995; Levitan et al., 1996; Wahsner et al., 1998 and further references therein). During two Russian Kara Sea cruises with RV "Professor Shtockman" in 1984 and RV "Dmitry Mendeleev" in 1993 (Lisitsyn and Vinogradov, 1995) surface samples were taken and investigated for grain-size and clay-mineral distribution (Fig. 1). Results were published by Shelekhova et al. (1995), Levitan et al. (1996), and Gorbunova (1997). These studies led to a division of the Kara Sea into different facies provinces. A synthesis paper concerning clay-mineral distributions in the central Arctic Ocean and the Eurasian shelf areas was published by Wahsner et al. (in press). They described an enrichment of smectite in surface sediments of the eastern Kara Sea compared to the clay-mineral composition of other Eurasian shelf sediments. Gurevich (1995) summarised a comprehensive data base derived from detailed sedimento-logical, mineralogical and geochemical studies of sediments from the western Eurasian Arctic shelf to explain the sedimentogenesis and the environmental settings. The grain-size distribution varies strongly (Levitan et al., 1996; Gurevich, 1995) even in small areas and therefore requires more detailed sampling, especially in the eastern Kara Sea.

Thus, surface sediments were taken during the 28th cruise of RV "Akademik Boris Petrov" in 1997 (Matthiessen et al., 1998) along four transects (Ob, Gydanskii, Yenisei, and 74°N) for sedimentological and clay-mineralogical analyses (Fig. 1). Additionally, water samples were taken at 5 stations along two transects (Ob and Yenisei rivers) to compare surface sediments and suspended matter transported by the Ob and Yenisei rivers (Müller, 1998). Mineralogical investigations using X-ray diffraction were carried out both on the clay fractions of the surface sediments and the suspended matter to get further information about the origin of Kara Sea sediments.

Methods

For disaggregation and removal of organic matter bulk sediment samples were shaken in a solution of hydrogen peroxide (10%). Sand and gravel (grain sizes >63 µm and >2 mm, respectively) were separated by wet sieving. Silt (2-63 µm) and clay (<2 µm) fractions were divided by a Stoke's law settling method in Atterberg tubes. To calculate the grain-size distribution all fractions were weighted after drying. Water samples were already centrifugated on bord to separate the suspended matter (Müller, 1998). The extracted sediments were also shaken in a solution of hydrogen peroxide (10%) to remove the organic matter. Because of low sediment amount we did not separate grain sizes >2 µm by the Stoke's law settling method. According to Lukashin et al. (this volume), who investigated the suspended matter for the granulometric composition, the maximum grain size does not exceed 10 µm and at least 80% of the suspended matter consists of clay fraction <2 µm.

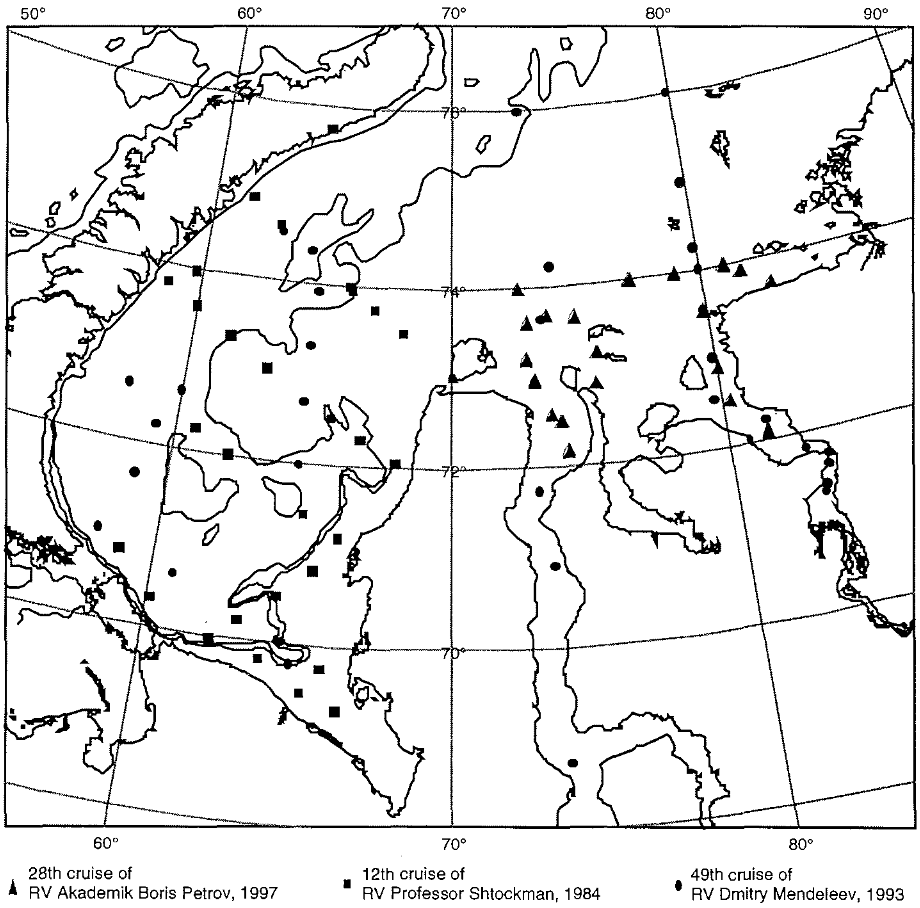

Fig. 1. Sampling stations of different Kara Sea cruises.

The clay fractions of both the surface sediments as well as the suspended matter were prepared for X-ray diffraction (XRD). As an internal δ-spacing standard 1 ml of a 0.4 % molybdenite suspension was added to a 40 mg clay sample. This mixture was dispersed and sucked onto a membrane filter (pore diameter 0.15 µm) by vacuum filtration to get high orientation of the clay minerals. After vaporisation with ethyleneglycol for about 24 h at 50°C the samples were measured between 2-40° 2θ with a step size of 0.02° 2θ/s and between 28 and 30.5° 2θ with a step size of 0.005° 2θ/s. The measurements were carried out with a Philips goniometer (PW1820) equipped with an automatic divergence slit, using CoKα radiation (40 kV, 40 mA). The following peaks were used to identify clay minerals: 17 Å for smectite, 10 Å and 5 Å for illite, and 7 Å for kaolinite plus chlorite. To differentiate kaolinite and chlorite we used intensity ratios of the 3.58 Å-kaolinite peak and the 3.54 Å-chlorite peak, identified by slow scan. Relative clay-mineral contents were calculated by using empirical factors after Biscaye (1965) and added to 100%.

All results are listed in Appendix 1 and Table 1. Additionally, grain-size and clay-mineral data from surface samles obtained on cruises of RV "Professor Shtockman" and "Dmitry Mendeleev" (Wahsner et al. 1998) are shown in the figures.

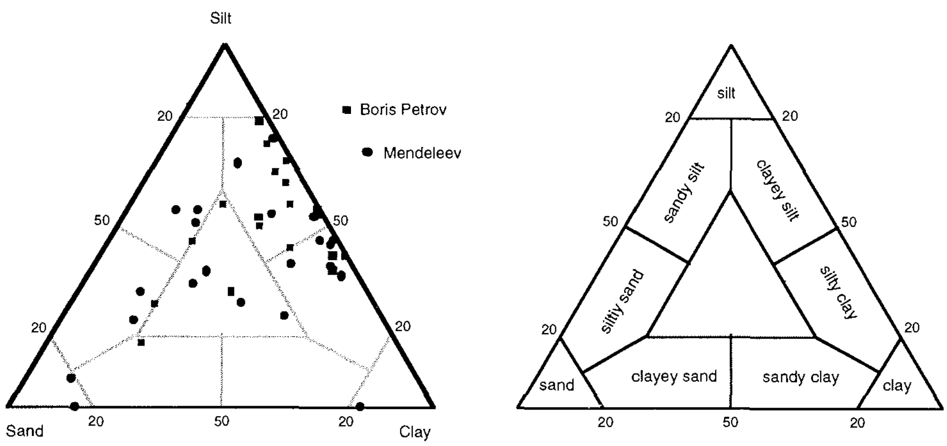

Fig. 2. Grain-size distribution of surface sediments from the Kara Sea. Data from Mendeleev cruise from Levitan et al. (1996).

Results

The grain-size composition varies strongly between silty clays and silty clayey sands (Fig. 2). Highest sand contents occur in the northern part of the study area (73°-74°N) in larger water depth (station BP97-39,-42,-58) (Fig. 3). In the Ob River sediments are more fine-grained in the southern part (station BP97-10 and -12). Towards the north clay and silt contents decrease (from station BP97-48 to -52) whereas sand-sized grains become more abundant. Sediments of the Yenisei River are characterized by a decrease of silt contents from the south to the north of the transect. In sediments of the eastern part of the 74°N transect clay contents partly increase up to 60% (station BP97-19,-21,-27,-43, and -46).

The clay fraction of the surface sediments is characterized by relatively high smectite contents of > 35% (Fig. 4). Maximum smectite contents of up to 50% occur in surface sediments of the 74°N transect (Fig. 5). The content of illite ranges between 20-30%; highest amounts occur in sediments of the Ob River. Chlorite and kaolinite are only of minor importance because of low amounts as well as low variation. Their contents range from 14 to 20% and from 12 to

15%, respectively (Fig. 4). The clay-mineral distributions of the suspended matter and the surface sediments show similar trends; however, they are different in absolute numbers (Fig. 4, Table 1). Smectite is enriched in suspended matter which contains up to 20% more smectite especially in the Ob River than the underlying surface sediments. In comparison, the contents of the other clay minerals are lower.

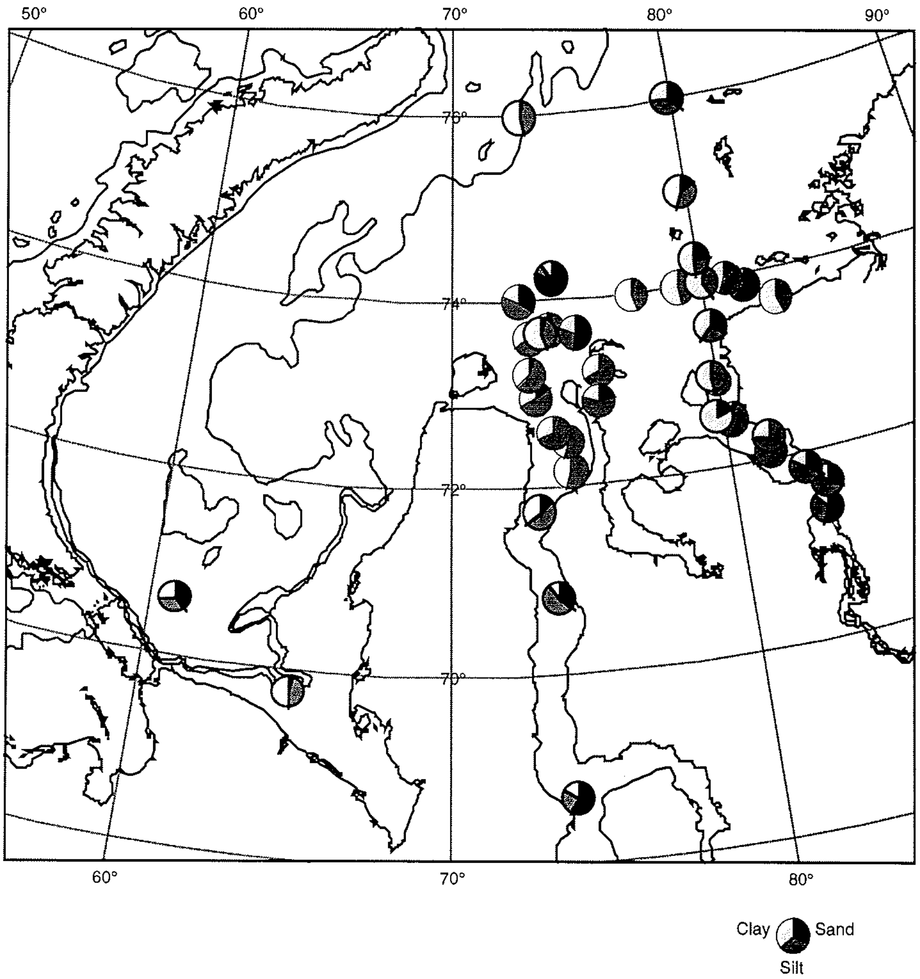

Fig. 3. Grain-size composition of surface samples of the Kara Sea.

Discussion

Previous studies of surface sediments led to a division of the inner Kara Sea into two facies provinces (Levitan et al., 1996): the Western Kara Sea province and the Ob-Yenisei province. Our study area which belongs to the Ob-Yenisei province shows no clear distribution pattern of sand-sized grains along or between different transects. For each grain-size fraction small-scale variations are obvious (Fig. 3). Generally, the grain-size composition of river and shelf sediments is related to the bottom relief as well as to the velocity of near-bottom currents. Gurevich (1995) also described a patchy distribution of all grain sizes. In addition, direct sediment input from the mainland and several sand banks and shallow areas influences the terrigenous sediment supply (Fig. 3). Near-bottom currents are responsible for resuspension and redeposition of the sediments in deeper areas where highest sand contents occur (App. 1). Levitan et al. (1995) described surface sediments from the inner Kara Sea which are of pre-Holocene age. Therefore some locations of our study area might also lack recent sediments because of winnowing and erosion. The flocculation of suspended and dissolved matter within the so-called "marginal filters" (the mixing zone of river and sea water) was already described by Lisitsyn (1995). Different processes lead to the deposition of 90-95% of the suspended matter in this small area (Lisitsyn, 1995). An expected increase, even though low, of fine-grained material in the mixing zone of river and sea water was also observed in our surface sediments.

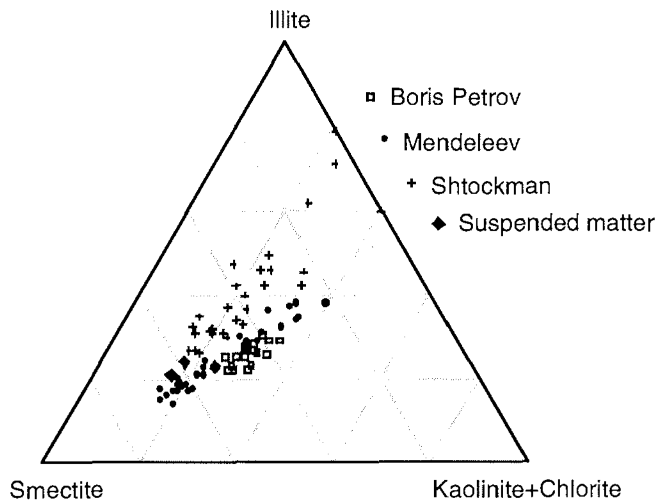

Fig. 4. Clay-mineral distribution of surface sediments from the Kara sea. Data for RV "Mendeleev" and RV "Shtockmann" samples are taken from Shelekova et al. (1995), Levitan et al. (1996), and Gorbunova (1997).

The clay-mineral distribution (Fig. 5) is mainly influenced by the mineralogical composition of the supplied material. As already described by several authors (e.g. Wahsner et al., 1998 and further references therein) smectite is a main clay mineral in surface sediments of the eastern Kara Sea compared to other Eurasian shelf sediments. Smectite derives from weathering products of the huge plateau-basalt complexes and their tuffs of the Putorana Mountains in West Siberia (Duzhikov and Struhnin, 1992). The distribution pattern shows maximum smectite contents north of the estuaries probably caused by the "marginal filter effect". The smectite contents in the suspended matter are significantly higher than in the surface sediments (Table 1). This enrichment of smectite is possibly caused by a selective non-sedimentation due to the capacity of cation exchange (Lisitsyn, 1995). Therefore smectite can be transported over longer distances compared to the other clay minerals. As already described by Wahsner et al. (1998) abundances of clay-minerals vary between different investigators (see also Fig. 4). This is probably caused by different grain-size definitions of the clay fraction (<1μm and <2μm, resp.) and different preparation and/or calculation methods. Hence, we calculated generally lower smectite contents (up to 10% difference) than some Russian colleagues (Shelekhova, et al. 1995; Levitan et al., 1996). The contents of the other clay minerals are therefore relatively increased. In contrast, clay-mineral data published by Gorbunova (1997) showed less smectite contents. Because smectite is the smallest of the clay minerals (e.g. Ehrmann et al. 1992) it is therefore enriched in the fractions <1μm compared to the fractions <2μm. Nevertheless, each data set shows the same trend and point to the eastern Kara Sea as the main source area of smectite.

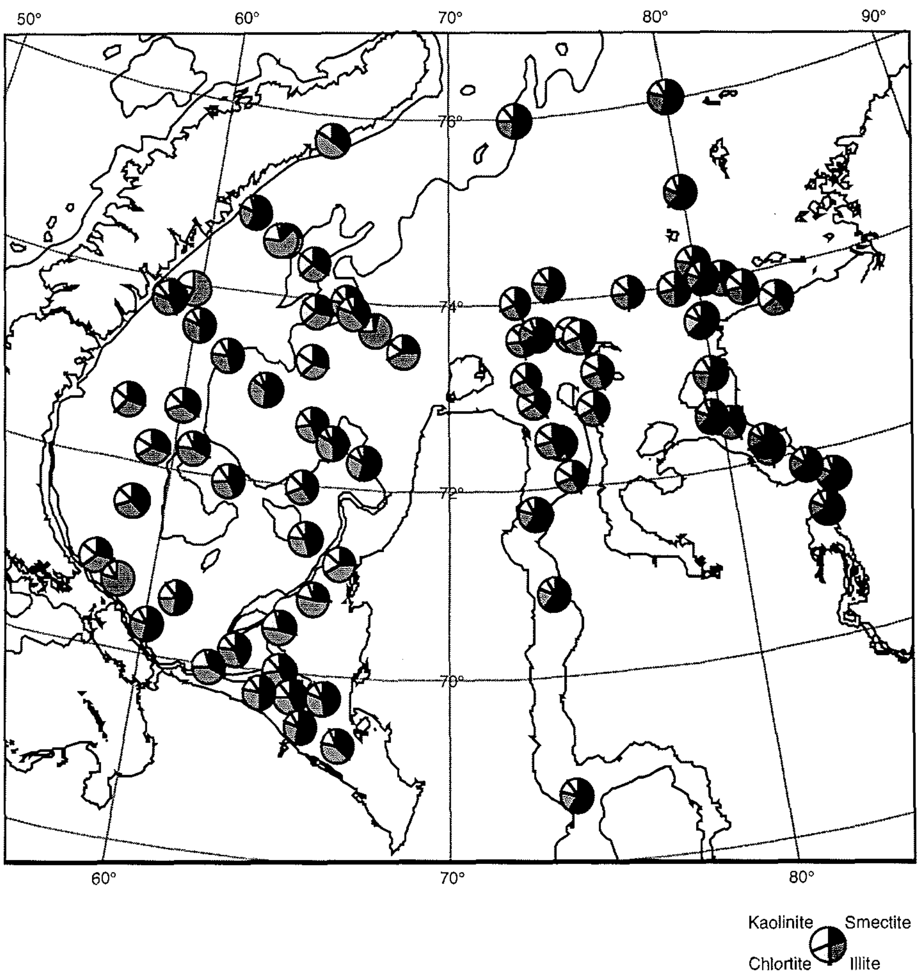

Fig. 5. Clay-mineral composition of surface samples of the Kara Sea.

Table 1. Comparison of the clay-mineral distribution in surface sediments and suspended matter. Please note that we compared the surface sediment of station BP97-35 with the suspended matter of station BP97-30 which is next to the BP97-35 location.

Sample	.Surface sediments				Suspended matter			
	Smectite	Illite	Kaolinite	Chlorite	Smectite	Illite	Kaolinite	Chlorite
BP97-10	43	27	14	15	63	21	8	9
BP97-17	44	27	14	15	59	24	8	9
BP97-35	40	25	19	15				
BP97-30					53	23	10	14
BP97-32	46	22	14	18	53	23	11	14

The clay-mineralogical composition of Ob and Yenisei River sediments are similar (Fig. 5, Table 1). The sediments from the Yenisei River, however, contain more clinopyroxene compared to surface sediments from the Ob River (Silverberg, 1972; Levitan et al., 1996; Vogt, 1997). The differences between clay mineralogy and the composition of the heavy mineral fraction in Ob and Yenisei River sediments are very interesting because smectite and pyroxene are believed to have the same source area (sheet basalts of the Putorana Mountains). The Ob River, however, does not drain the Putorana mountains or the surrounding tuff deposits (Okulitch et al., 1989). Therefore, it would be surprising if Ob and Yenisei River sediments had the same mineralogical composition. Thus, the significant amount of smectite in Ob River sediments may result from the erosion of other smectite-bearing deposits containing a low pyroxene content. Shelekhova et al. (1995) and Levitan et al. (1996) described sediments from the southwestern part of the Kara Sea containing 30-40% smectite. Its probable source area is in the Barents Sea whereas a supply from the Putorana Mountains is not very likely.

Unfortunately, sampling stations in the northeastern Kara Sea are rare. Samples out of this area would complete existing mineralogical distribution maps and would allow to follow the transport pathways of the supplied material.

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Appendix 1: Grain-size and clay mineral composition of surface sediments.

Latitude	Longitude	Station	Depth (m)	Sand %	Silt %	Clay %	Smectite %	Illite %	Chlorite %	Kaolinite %
Ob-Transect										
72.170	74.294	BP97-12	13	0	55	45	42	28	15	15
72.503	74.081	BP97-10	15	1	53	46	43	27	15	14
72.584	73.749	BP97-47	18	1	68	31	43	28	15	14
72.689	73.731	BP97-17	20	5	65	30	44	27	15	14
72.961	73.148	BP97-48	29	15	52	32	38	29	18	15
73.210	72.895	BP97-49	29	6	56	38	39	30	17	14
73.611	72.951	BP97-50	28	16	50	34	49	25	14	12
Suspended matter (Ob River)										
		BP97-10					63	21	8	9
		BP97-17					59	24	8	9
Gydanski Bay-Transect										
72.890	75.483	BP97-56	14	22	56	22	42	26	17	15
73.224	75.619	BP97-55	14	4	62	34	45	25	16	14
73.650	74.839	BP97-58	23	52	29	20	45	27	16	13
Yenisey-Transect										
72.093	81.481	BP97-32	10	2	79	19	46	22	18	14
72.509	80.329	BP97-35	14	3	72	24	40	25	19	15
72.889	80.093	BP97-27	19	1	53	46	45	23	17	15
73.536	79.918	BP97-39	40	32	32	36	49	23	16	12
Suspended matter (Yenisey River)										
		BP97-30					53	23	10	14
		BP97-32					53	23	11	14
Kara Sea, 74°N-Transect										
74.000	72.662	BP97-52	30	34	46	20	43	27	17	14
73.999	77.204	BP97-46	27	5	38	57	50	22	15	13
74.001	79.025	BP97-19	30	3	42	55	49	23	16	12
74.001	81.008	BP97-21	41	12	44	44	47	25	16	12
73.899	81.667	BP97-42	32	60	18	22	49	22	16	13
73.709	82.813	BP97-43	31	0	42	58	36	29	20	15

HEAVY METALS IN BOTTOM SEDIMENTS FROM THE ESTUARIES OF THE RIVERS OB AND YENISEI

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Introduction

During the expedition to the Kara Sea with RV "Akademik Boris Petrov" in September 1997 an extensive sampling program was conducted in the estuaries of the rivers Ob and Yenisei in order to analyse the chemical composition of bottom sediments, in particular the content of heavy metals (Krasnyuk, 1998). Due to the location in the marginal filter zone of Ob and Yensei complex interactions between water column and sediments occur, of which the deposition of chemical elements is an important process (Lisitzyn, 1995). Therefore, the analyses of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Ba and Pb in the upper 2 cm of sediments allows to evaluate the spatial variability of the chemical composition of recent sediments in the study area. In particular, the relationship of distribution pattern to the marginal filter should be addressed as well as the influence of dynamic processes in the water column on dispersal and deposition of heavy metals.

Material and Methods

The chemical composition of 36 surface sediment samples (sampling interval 0-2 cm) and 27 samples from the sediment cores (GKG, MUC) taken at stations 1, 12 and 47 were studied during the cruise. The first results of these investigations are described in the cruise report (Krasnyuk, 1998). This paper presents the initial results from onboard analyses of chemical elements in surface sediments which are listed in Appendix 1. The results of the sediment core investigations will be published elsewhere.

The chemical composition of bottom sediments was analysed after sediments were dried at 105°C and powdered to 50-100. The contents of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Ba and Pb were determined by X-ray-fluorescence analysis using the automated X-ray spectrometer SPARK-1. Samples were analyzed in cells of 0.25 cm^3 size. Calculations of concentrations were performed by normalizing the data to external standards. The state samples CDO-1 (terrigenic clay), CDO-2 (volcanic-terrigenic mud), CDO-3 (calcareous mud), CDO-8 (siliceous mud) and CDO-9 (red ooze) were taken as standards. The selected equations of dependence between measured intensities and element contents take into account the clusters located around the analytical line. The used exposition results in a statistical error of analysis of 1-5%. These conditions allow to carry out the analysis with an error of less than 30% for concentrations close to the detection limit.

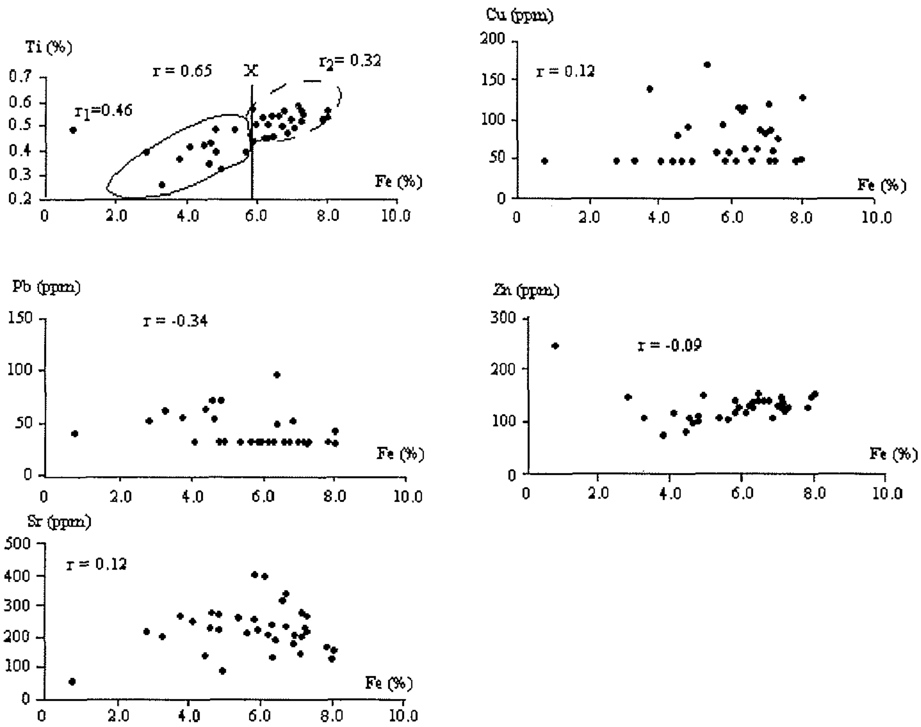
Table 1. Statistical parameters of the distribution of chemical elements in the surface sediments from the Kara Sea (28th cruise of RV " Akademik Boris Petrov").

Parametres	Fe %	Mn %	Ba %	Ti %	V ppm	Cr ppm	Ni ppm	Co ppm	Cu ppm	Zn ppm	Pb ppm	Rb ppm	Sr ppm	As ppm	Br ppm
CEC	4.65	0.10	0.065	0.45	90	83	58	18	47	83	16	150	340	1,7	2,1
CS	3.33	0.067	0.080	0.45	130	100	95	20	57	80	20	200	450	6,6	6
CBS	6.5	0.67	0.23	0.46	120	90	225	74	250	165	80	110	180	13	70
X1994	4.94	0.119	0.0558	0.452	139	96	59	18		96			312		
PF1993	7.0	0.3939	0.0617	0.467	115	76	79	30		170			402		
IF1969	5.2	0.220	0.04	0.350		155	66	23		540					
X (N=36)	5.838	0.307	0.0426	0.471	100.1	93.1	51.6	27.8	74.3	127.7	41.0	80.0	222.8	39.2	73.3
X1 (N=14)	4.271	0.189	0.0414	0.399	75.9	84.3	34.9	20.6	75.9	120.0	47.1	68.0	211.7	35.0	63.2
X2 (N=22)	6.835	0.383	0.0433	0.517	115.4	98.7	62.3	32.4	73.3	132.6	37.1	87.7	229.8	41.9	79.7
S	1.576	0.186	0.0056	0.077	30.6	23.2	18.3	7.6	32.0	27.8	15.6	27.8	72.7	16.8	34.3
S1	1.315	0.082	0.0063	0.064	33.9	29.0	11.3	5.4	38.7	41.9	15.6	34.5	67.9	17.6	30.6
S2	0.625	0.196	0.0050	0.042	14.6	17.0	13.2	4.6	27.8	11.7	14.6	19.8	76.3	16.1	35.7
t-criterium	3.95*	4.14*	1.06	3.88*	3.19*	1.73*	4.16*	4.06*	0.24	1.1	2.12*	1.94*	0.97	1.39	1.85

Note: CEC, CS, CBS - clarks of chemical elements: CES - earth's crusts, CS - sedimentary rocks (clays), CBS - deep-water clays;
X1994 -Holocene muds of the Kara Sea (Gurvich et al.,1994);
PF1993, PF1969 - composition of the suspension from the Ob Bay in autumn 1993 (PF1993) and spring 1969 (PF1969);
X, X1, X2 - average contents of chemical elements in the surface sediments, calculated for all samples (X), for the first (X1) and the second (X2) geochemical types; N - number of samples analysed;
S, S1, S2 - dispersions of the contents of chemical elements in the surface sediments, calculated for all samples (S), for the first (S1) and the second (S2) geochemical types; t-criterium - values of Student t-criterium (*- statistically important differences at 95% confidence level).

Results and Discussion

Statistic parameters of the distribution of chemical elements in the surface sediments and clarks for different rock types are presented in Table 1. The surface sediments of the study area are rich in elements such as Fe, Mn, Cu, Zn, Pb, As and Br relative to both the average composition of the Earth's crust and clarks of the sedimentary rocks. Most studied samples differ much from the average composition of deep-water clays because they are depleted in most elements. This reflects the geological structure of the catchment area of Ob and Yenisei, which are tundra and taiga landscapes with permafrost. Thus, high contents of Fe and Mn in the muds are related to their accumulation in dead plants. Then, owing to low activity of microorganisms under low temperatures, dead plants are accumulated at the soil surface and are washed into the rivers in spring (Lisitsyn, 1995). Elevated contents of Cu, Zn, Pb, As and Br are primarily related to the presence of large copper-pyrite and copper-zink deposits, ores of the Siberian trapp basalts and rocks of the Taimyr Peninsula which are characterized by granitophylic associations of chemical elements.



X - average content of ferrum (5.838), calculated for all samples;
element contents in samples with Fe < 5.838%;
element contents in samples with Fe > 5.838%;
r, r_1, r_2 - correlation coefficients, calculated for all sample (r), for samples with Fe < 5.838% (r_1) and for samples with Fe > 8.838% (r_2).

Fig. 1. Contents of iron and other elements in bottom sediments from the Ob and Yenisei estuaries.

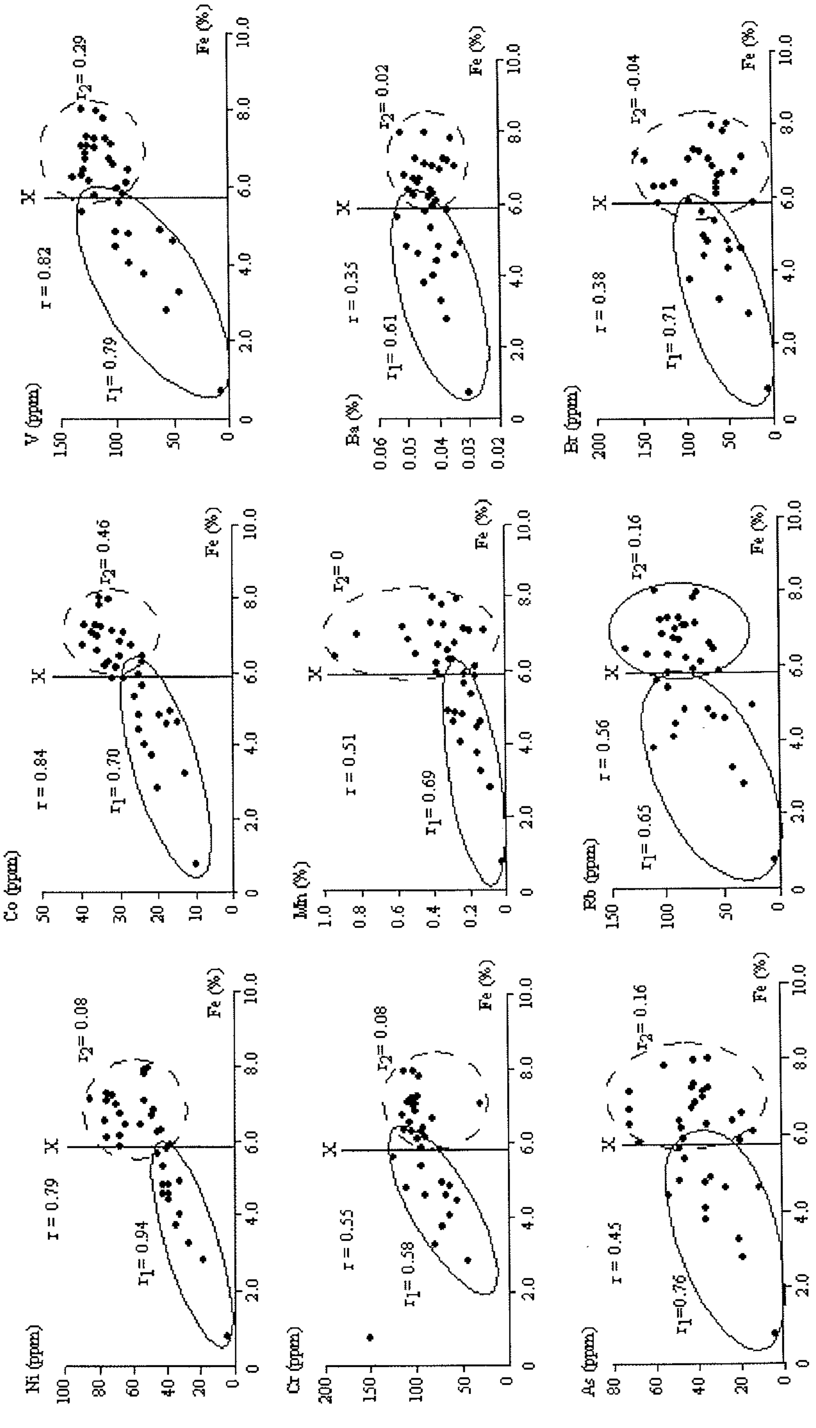


Fig. 1 (cont´d.). Contents of iron and other elements in bottom sediments from the Ob and Yenisei estuaries.

The large difference in chemical composition between the surface sediments from the Ob and Yenisei estuaries and the oceanic sediments (red oozes) shows that the sediments were formed in the shallow littoral zone of the inner shelf. The main parameter responsible for the variability is iron which is characterized by a bimodal distribution curve. Prominent are two maxima with the average contents of 6,635% and 4,271%, respectively; the differences being statistically important. Thus, the relationship between the variable contents of Fe and other elements will be considered in more detail.

The analysis of the contents of Fe and associated chemical elements revealed two different sediment groups (Fig. 1): the first one with Fe > 5,838% (average content, Table 1) and the second one with Fe < 5,838%. Each group is characterized by statistic significant distribution of elements and correlation dependencies (Table 1, Fig. 1). The correlation between the contents of chemical elements and the two sediment groups, tested by the Student t-criterion, revealed that most elements show statistically important differences. The differences are statistically insignificant only for Ba, Cu, Zn and Sr. The sediment group with low contents of Fe also shows high values of dispersion of the contents of chemical elements (Table 1).

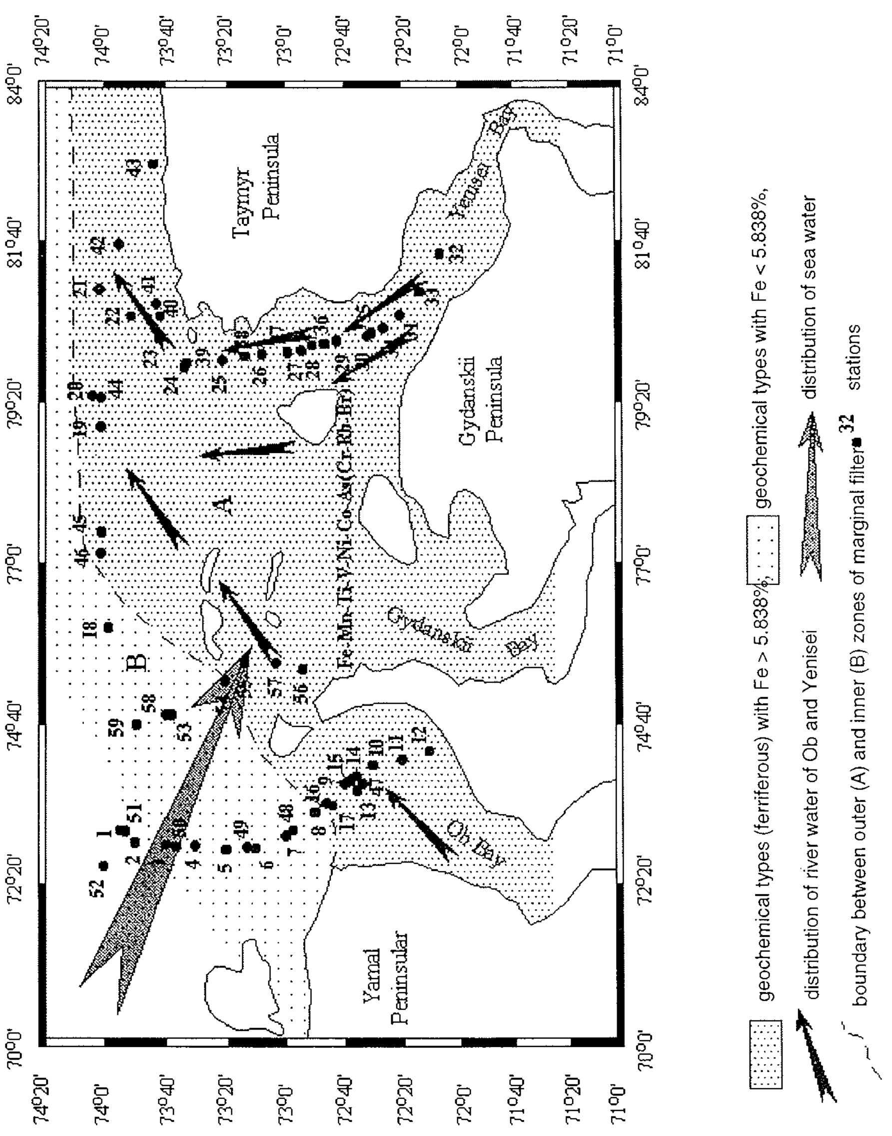
It is interesting to note that the chemical composition of sediments with Fe > 5,838% correspond to the suspension from the Ob Bay (Table 1) described by Gurvich et al. (1995).

Two groups of elements can be distinguished because of the character of correlation with Fe (Fig. 1). The first group includes Co, V, Ni, Ti, Cr, Rb, Mn, As, Br and Ba and shows a high statistically significant correlation with Fe. The second group includes Zn, Cu, Sr and Pb and shows low insignificant or negative correlation (Pb) to Fe (Fig. 1). The first group of elements is positively correlated with sediments with low contents of Fe (<5,838%), whereas it is statistically insignificant correlated with sediments with high contents of Fe (>5,838%) (Fig. 1). Cobalt showing high correlation coefficients with Fe for both the first and the second sediment group is the exception.

The regional distribution of the two sediment groups in the investigation area of the Ob and Yenisei estuaries is shown in Figure 2. A well-defined zonation is observed: The inner zone presented mainly by sediments with high contents of iron (>5,838%) is replaced northwestward by sediments with low contents of iron (<5,838%). The observed zonation corresponds to the distribution of river waters in the marginal filter zone of Lisitsin (1995).

Thus, two geochemical types of sediments can be clearly distinguished based both on absolute contents of chemical elements and the structure of their correlation with Fe. The first type is characterized by high contents of Fe, Mn, Ti, V, Cr, Ni, Co, Rb, Br and As and by the lack of any correlation between these elements and Fe (excluding Co). This type is spatially confined to the inner zone of the marginal filter characterized by subsaline waters with maximum influence of fresh waters (Fig. 2). The main process responsible for the composition of these sediments is their mechanical differentiation that is supported by the lack of correlation coefficients between elements in this geochemical sediment type.

Fig. 2. Distribution of geochemical types in the surface sediments from the Ob and Yenisei estuaries



The second geochemical type of surface sediments with low contents of Fe, Mn, Ti, V, Cr, Ni, Co, Rb, Br, As and significant positive correlation with Fe reflects sedimentation in the marine environment where chemical elements are accumulated due to their sorption from sea water by Fe and Mn hydroxides. This type occurs in the outer zone of the marginal filter where saline waters are associated with low suspension concentrations (cf. Lukashin et al., this volume).

The zonation of geochemical types in the surface sediments distinctly reflects the influence of Yenisei water which is drifting westward, and the penetration of sea waters into the Ob Bay. Therefore, the first geochemical type of the surface sediments has a widespread westward distribution.

The regular distribution of Pb, Cu and Zn, their absolute values (increased values relative to clarks), and the absence of any correlation with Fe in surface sediments of the study area may indicate different sources of these elements, and their presence in water mainly in dissolved form.

Conclusions

1. The surface sediments show a well-defined Cu-Zn-Pb-As geochemical specialization caused by specific chemical composition of material supplied by the Ob and Yenisei catchment area and by erosion of bedrocks on Taimyr Peninsula.

2. Two geochemical types of surface sediments are distinguished reflecting different processes of formation in their composition. Processes of mechanical differentiation play an important role in the formation of the first (ferruginous) type with high contents of Mn, Ti, V, Cr, Ni, Co, Rb, Sr and without any correlation between these elements and Fe. Low contents of chemical elements and their positive correlation with Fe which is characteristic of the second geochemical type are related to marine sedimentation conditions.

3. The spatial distribution of the geochemical types of surface sediments corresponds to the marginal filter structure of the Kara Sea (Lisitsyn, 1995) where hydrological and hydrochemical parameters of waters influence the distribution, in particular by considerable westward drift of transformed waters from the Gulf of Yenisei. Therefore, the spatial boundary between geochemical types reflects the transition between the inner zone of the marginal filter (the first geochemical type) and the outer zone (the second geochemical type).

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Appendix 1. Chemical composition of surface sediments.

St.	Core Depth cm	Ba %	Ti %	V ppm	Cr ppm	Mn %	Fe %	Co ppm	Ni ppm	Cu ppm	Zn ppm	As ppm	Pb ppm	Br ppm	Rb ppm	Sr ppm
1	0-2	0.044	0.43	120	75	0.17	5.82	29	41	94	140	68	<40	130	98	256
8	0-2	0.040	0.48	89	64	0.24	4.82	25	40	91	109	49	<40	51	62	270
9	0-2	0.048	0.50	105	85	0.37	6.71	27	49	65	141	72	<40	58	89	237
10	0-2	0.052	0.56	130	114	0.41	8.00	35	51	130	153	35	43	52	110	160
12	0-2	0.044	0.53	116	104	0.28	7.97	33	53	<60	146	42	<40	66	72	126
15	0-2	0.036	0.52	110	98	0.35	7.84	35	54	<60	126	56	<40	55	77	168
17	0-2	0.042	0.50	98	94	0.39	5.93	25	39	60	126	47	<40	96	76	223
18	0-2	0.038	0.39	55	44	0.08	2.82	20	18	<60	147	19	52	26	30	218
19	0-2	0.035	0.49	130	31	0.12	7.10	29	54	120	127	72	<40	73	87	200
21	0-2	0.042	0.50	130	106	0.31	6.30	24	44	110	136	35	<40	133	116	236
24	0-2	0.043	0.44	123	92	0.38	6.20	34	68	<60	130	48	<40	62	84	207
25	0-2	0.042	0.49	126	103	0.20	7.10	37	75	85	144	37	<40	94	85	148
27	0-2	0.039	0.52	118	103	0.82	7.00	36	70	83	130	37	<40	144	92	204
28	0-2	0.038	0.56	108	106	0.35	7.26	39	76	<60	130	35	<40	85	98	220
30	0-2	0.044	0.59	105	109	0.22	7.15	32	86	<60	135	38	<40	36	74	280
31	0-2	0.037	0.57	94	95	0.23	5.85	32	68	<60	117	20	<40	22	53	403
32	0-2	0.041	0.53	90	100	0.17	6.12	31	75	<60	117	14	<40	62	70	391
33	0-2	0.047	0.54	103	108	0.32	6.58	36	77	<60	141	19	<40	61	61	318
34	0-2	0.047	0.56	127	115	0.28	6.73	40	68	63	140	43	<40	42	93	340
36	0-2	0.047	0.55	124	99	0.41	7.30	36	75	74	127	42	<40	90	89	268
37	0-2	0.037	0.52	118	106	0.56	7.23	35	73	60	122	43	<40	157	104	227
42	0-2	0.043	0.48	130	94	0.19	5.38	26	43	170	106	46	<40	67	98	260
43	0-2	0.050	0.54	129	114	0.94	6.42	30	65	64	153	49	49	112	136	190
46	0-2	0.048	0.44	139	96	0.29	6.29	33	45	114	128	73	<40	124	99	140
47	0-2	0.051	0.47	127	101	0.53	6.87	30	49	86	107	41	52	67	105	179
48	0-2	0.050	0.39	100	110	0.28	4.82	20	43	90	99	36	72	75	85	227
49	0-2	0.053	0.39	97	127	0.22	5.65	24	46	60	103	49	<40	82	109	213
50	0-2	0.041	0.42	101	59	0.16	4.44	25	40	<60	79	54	62	78	92	142
51	0-2	0.035	0.34	47	70	0.13	4.59	18	40	81	104	11	71	49	47	228
52	0-2	0.045	0.36	76	73	0.16	3.78	22	35	140	75	36	55	95	110	271
53	0-2	0.042	0.41	88	65	0.24	4.07	24	34	<60	118	36	<40	51	94	253
54	0-2	0.033	0.32	60	74	0.32	4.92	17	34	<60	148	34	<40	77	24	90
55	0-2	0.042	0.45	89	93	0.49	6.42	24	56	115	142	23	97	63	59	190
56	0-2	0.047	0.43	50	92	0.29	4.64	15	42	<60	100	27	53	36	57	275
58	0-2	0.039	0.26	44	80	0.13	3.27	13	28	<60	108	21	62	61	41	200
59	0-2	0.030	0.48	6	153	0.03	0.77	10	<6	<60	244	4	40	7	5	61

MAJOR AND MINOR ELEMENTS IN SURFACE SEDIMENTS OF OB AND YENISEI ESTUARIES AND THE ADJACENT KARA SEA

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Introduction

The Kara Sea is one of the broad shelf seas from which large quantities of sediment are transported via currents and drifting ice into the Arctic Ocean. This shelf region is mainly supplied by Ob and Yenisei rivers (Aagaard and Carmack, 1989). Despite this enormous outflow, concentrations of particulate matter are low in comparison to other rivers with similar water discharges (Bobrovitskaya et al., 1996) due to forests and swamps in context with permafrost in the hinterland as well as erosion resistant rocks of the Putoran mountains. The catchment area of the Ob River encloses the Western Siberian Lowland with its Quaternary sediments and the Altai mountains consisting mainly of metamorphic rocks (Dolginow and Kropatschjow, 1994). The latter one plays a minor role for the composition of particulate material in the Ob River near the mouth (Bobrovitskaya et al., 1996). The Yenisei River is draining the Western Siberian Lowland, too, but also the Putoran mountains with its trapp basalts (Duzhikov and Strunin, 1992).

Geochemical investigations are used to determine source areas of Arctic Ocean sediments. Particulate matter forming the sediments enters mainly through estuaries. Thus the surface sediments of estuaries reflect in principle the chemical composition of material a river adds to an ocean, depending on the element's chemical behaviour. It is expected that surface sediments of Ob and Yenisei rivers and their estuaries show different chemical compositions because of different source areas.

Sampling and methods

Surface sediment samples were taken in the Kara Sea and the estuaries of Yenisei and Ob rivers by Ocean Grab and multi corer, respectively, during expeditions of RV "Dmitriy Mendeleev" in 1993 and RV "Akademik Boris Petrov" in 1997 (Appendix 1). The first centimetre of the sediment was sampled. After drying and grinding samples were analyzed by X-ray fluorescence spectrometry (PW 2400 and PW 1400 with Rh-tube (Philips)) for their elemental concentrations. The results were checked with international reference standard samples (GSR 5 (shale) and "Alkaline Agpaite Granite" (granite)) and internal standard samples (TW TUC (shale) and Loess (loess soil)). Contents of determined elements in investigated surface samples are shown in Appendix 1.

Results and discussion

The origin of marine sediments can be determined by analyzing the elemental composition of the sediment because different source rocks show different chemical characteristics. On the other hand it has to be considered that elements vary in their behaviour, e.g. Fe is easily dissolved in river water, but it is flocculating with increasing salinity by entering the estuary (Chester, 1990; Lisitsyn, 1995). Zr, for example, is a major compound of the mineral zircon, which is very resistant against weathering, and disposed of a high density. To compare element contents of surface sediments from different locations they are related to their Al-content. Using element/Al-ratios dilutions by sand, clay minerals or organic compounds, for example, are corrected.

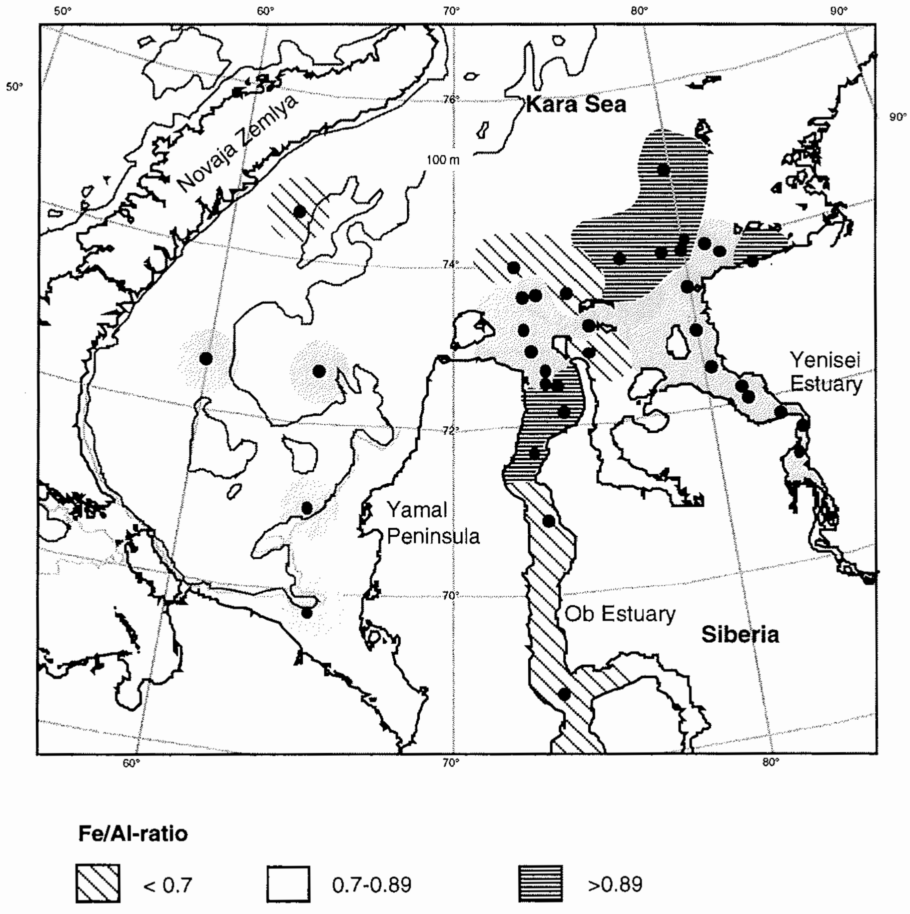

Fig. 1. Distribution of Fe/Al-ratios in surface sediments of the Ob and Yenisei estuaries and adjacent Kara Sea.

Ob and Yenisei estuaries

In the Ob estuary enhanced Fe/Al-ratios were determined in surface sediments at about 72° N (Fig. 1). After Müller and Stein (this volume) the grain size fraction < 2 mm increases up to 50 % of the whole sediment in this region indicating an increased accumulation of clay minerals. A major factor controlling this process is the salinity of water. In river water more Fe is dissolved than in saline water (Chester, 1990). In estuaries Fe flocculates as Fe-oxyhydroxides because of increasing salinity and therefore changing of physicochemical conditions in the water column. Hence there are zones in estuaries where sediments are rich in Fe-content. Near this area clay minerals and organic compounds are precipitating, too. According to Lisitsyn (1995) this zone is described as "marginal filter". North of this region the Fe/Al-ratio decreases, but is still higher compared to an average shale. Precipitated and resuspended Fe-oxyhydroxides are probably supplied by currents.

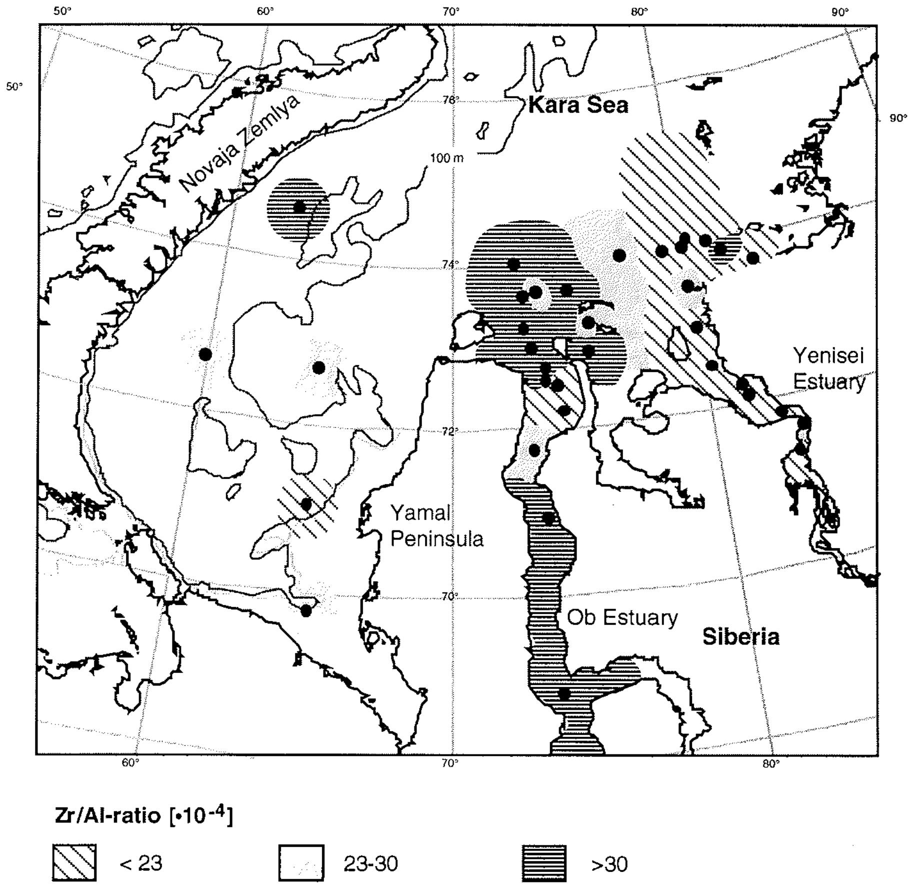

Fig. 2. Distribution of Zr/Al-ratios in surface sediments of the estuaries of Ob and Yenisei rivers and adjacent Kara Sea.

The Fe/Al-ratio in sediments of the Yenisei Rivers' estuary is enriched compared to an average shale probably due to Fe-rich source rocks in the hinterland. Along the transect between 71° N and 73° N the Fe/Al-ratio in the sediments varies between 0.7 and 0.88. Churun and Ivanov (1998) measured a salinity between 2 and 10 ppt in the surface water at about 73° N in Yenisei Estuary indicating the "marginal filter". This is supported by high concentrations of Fe in particulate matter between 73° N and 72.5° N in the upper water column of the Yenisei Estuary (Lukashin et al., this volume). Northwards a region with enhanced Fe/Al-ratios is explained by the occurrence of ferromanganese nodules and crusts (Fig. 1). Bogdanov et al. (1995) found at station Men 4399 ferromanganese nodules of variable composition. Thus some locations are richer in Fe, Mn or minor elements like Ni or Co, which are incorporated in the nodules.

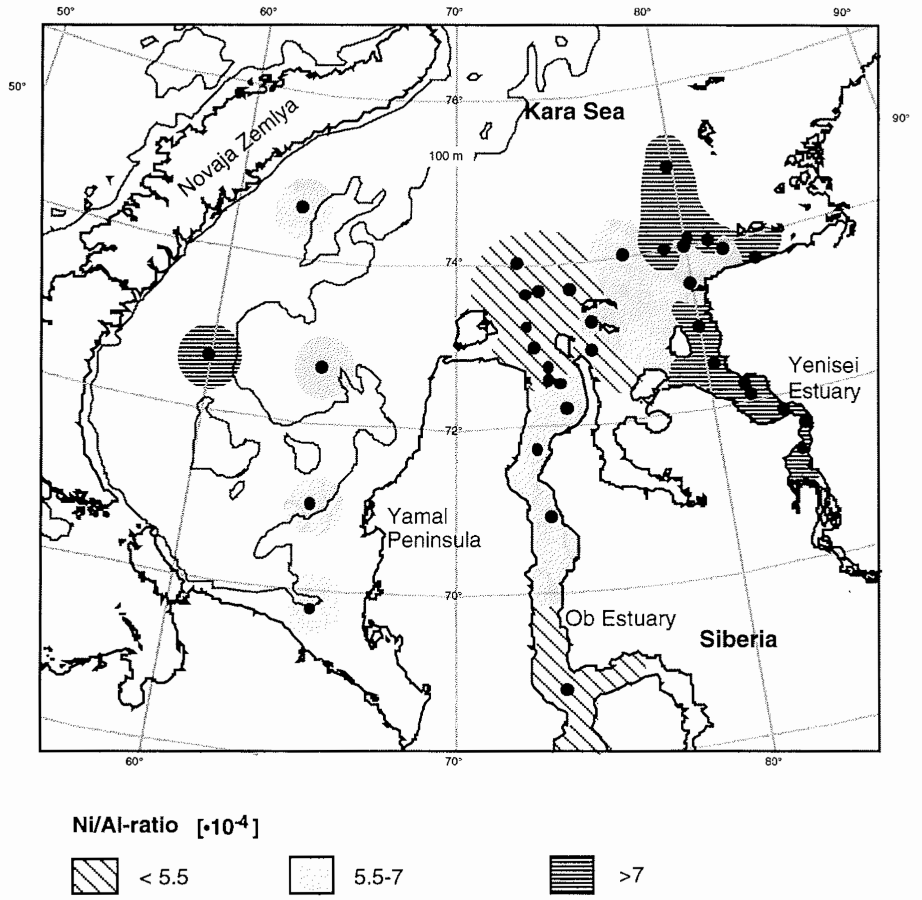

Fig. 3. Distribution of Ni/Al-ratios in surface sediments of the Ob and Yenisei estuaries and adjacent Kara Sea.

Zr and Si form heavy minerals like zircon or quartz, respectively. Their concentration in sediments is controlled by source rocks, grain size and current velocities. Zr/Al-ratios show a high variability in surface sediments due to different source areas and current velocities (Fig. 2). In sediments of the Yenisei Estuary the average Zr/Al-ratio is lower than in sediments of the Ob Estuary probably because of different source rocks in the hinterland. Si/Al-ratios show a similar distribution. Some sites in the Yenisei Estuary display a higher Zr/Al-ratio than the surrounding sites. This is explained by positions close to the coast line where more coarse-grained terrigenous material is deposited.

In the Ob Estuary the Zr/Al-ratio is enhanced in the southern part of the investigated area. In the "marginal filter" at about 72° N the Zr/Al-ratio is decreasing because of an increased supply of clay fraction. Grain size data of Müller and Stein (this volume) is supporting this interpretation. North of this zone the ratio is increased because of mixing with eroded material of surrounding shoals.

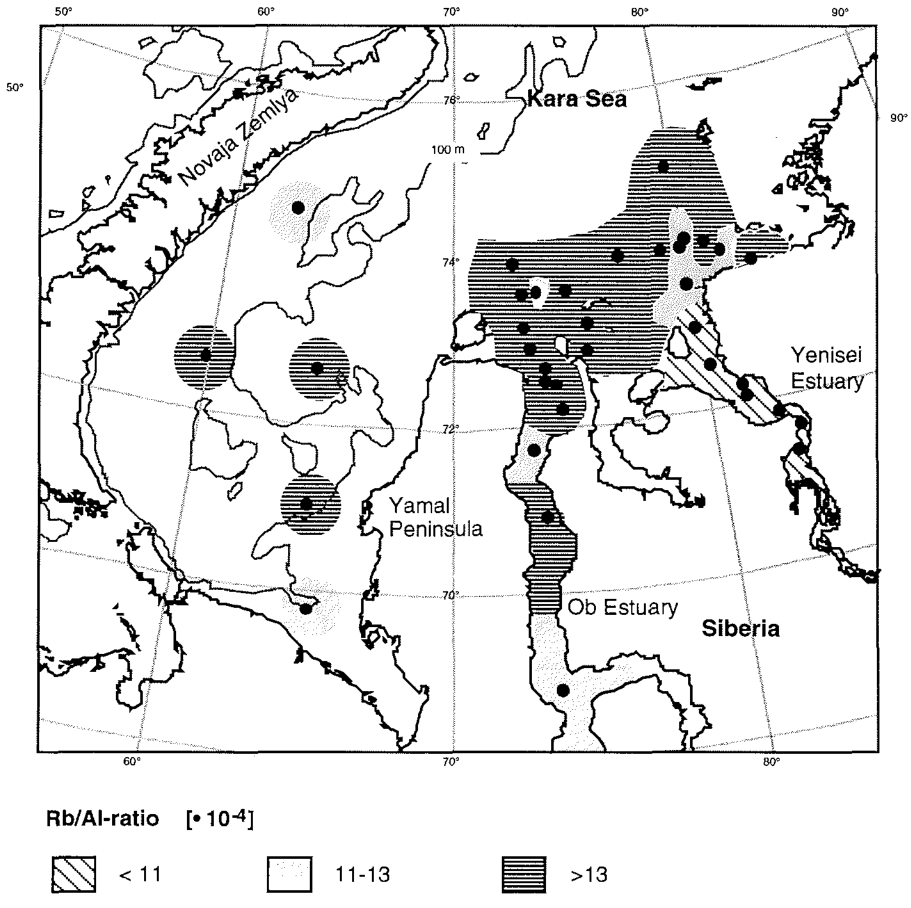

Fig. 4. Distribution of Rb/Al-ratios in surface sediments of the Ob and Yenisei estuaries and adjacent Kara Sea.

In Figure 3 the distribution of Ni/Al-ratios in surface sediments is shown. The sediments in the Yenisei Estuary have a higher Ni/Al-ratio than those in the Ob Estuary due to different sources in the catchment areas. Most of Ni has to be transported by particles because dissolved and colloidal concentrations of Ni are higher in the Ob than in the Yenisei (Dai and Martin, 1995). Sediments in the area between 73° N and 74° N of the Yenisei Estuary contain reduced Ni/Al-ratios. Probably most particulate matter and colloidal Ni are deposited before reaching this area. Towards the north and east the Ni/Al-ratios are increasing in the sediments due to ferromanganese nodules and concretions of variable Fe- and Mn-content (see above).

In the Ob Estuary Ni/Al-ratios in the surface sediments are similar to that determined in an average shale. North of this area sediments are enriched in Ni content because of scavenging with flocculating Fe-oxyhydroxides due to increasing salinity. Dai and Martin (1995) found a high concentration of dissolved and colloidal Ni in Ob River water. Larger quantities appear to be deposited in the Ob River's "marginal filter" than in a corresponding area of the Yenisei River. North of site BP 97-10 the Ni/Al-ratio in surface sediments is again similar to that of an average shale. Here material transported by the Ob River as well as resuspended sediment from surrounding shoals is deposited.

Rb's characteristics are similar to that of K. Thus Rb is able to replace K in minerals, and Rb concentrations are low in source rocks with low orthoclase content. Figure 4 shows Rb/Al-distribution in the study area. Between the sites Men 4409 and BP 97-39 (Yenisei Estuary) Rb/Al-ratios are especially low because of reflecting the geology of the hinterland. Presumably due to mixing of fresh and sea water and their particulate materials the Rb/Al-ratio is increasing in the sediments of the outer Yenisei Estuary. The shape of the Rb/Al-ratio-distribution confirm a northwards-directed current of fresh water from the Yenisei according to Lisitsyn (1995).

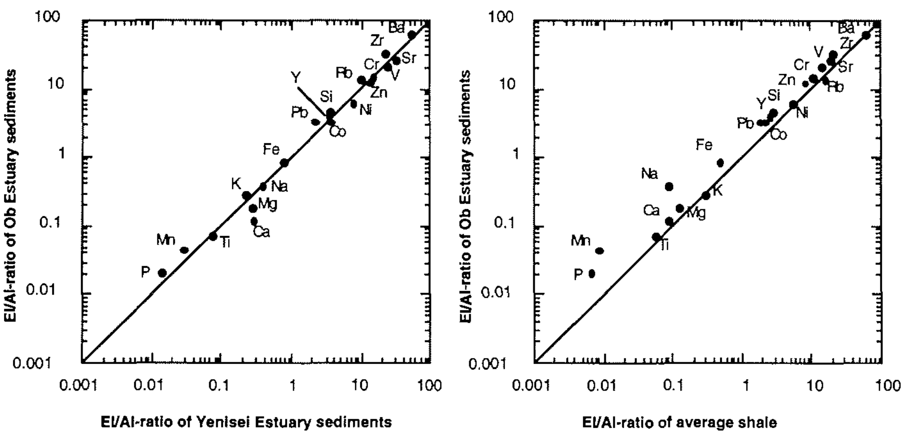

Fig. 5: a) Comparison of mean element (El)/Al-ratios of surface sediments of the Ob Estuary with those of the Yenisei Estuary (Data are given in Table 1); b) Comparison of mean El/Al-ratios of surface sediments with those of an average shale (Data are given in Table 1).

In the Ob River Rb/Al-ratios are enriched but not as high as in an average shale. Most of Rb in rivers is transported by particulate matter (Chester, 1990). Therefore the Quaternary sediments of the Siberian Lowland, i.e., the source area, contain reduced amounts of Rb compared with an average shale. In the outer Ob estuary the Rb/Al-ratio is enhanced in surface sediments which is probably caused by mixing of particulate matter of the river with eroded material from surrounding shoals.

The catchment areas of both rivers include the Siberian Lowland, the Yenisei River additionally drains the Putoran mountains. The latter one consists of trapp basalts showing a chemical composition (Lightfoot et al., 1990) which is different from that of continental crust or an average shale (Taylor and McLennan, 1985). Ni, Ti, Fe, and several other elements are enriched in these basalts, Rb, K, Si, and Zr are depleted in comparison to the average shale (Table 1). In Figure 5 element/Al-ratios of sediment samples from the Ob Rivers' estuary between 70° and 73° N are compared with those of sediment samples from the Yenisei Estuary between 71° and 73,5° N. Elements like Ca, Mg, Sr, and Ni are enriched in Yenisei Estuary sediments due to sediment supply from the trapp basalts from the Putoran mountains. The enrichments of Rb, K, Ba, Pb, Si, and Zr in sediments of the Ob Estuary are assumed as depletions in Yenisei Estuary's sediments because of dilution of its particulate matter supplied from Western Siberian Lowland with material from the Putoran mountains.

Comparing mean element/Al-ratios of Ob Estuary sediments with the element/Al-ratios of an average shale (Fig. 5), most of the measured elements are enriched in the surface sediments. Several elements are directly transported from the coastal areas, like Si, Zr, and Ti, while other elements, e.g. Fe, Mn, and P, are flocculated due to increasing salinity. The depletion of K and Rb in context with enhanced concentrations of Cr, V, Zn, Ca, Mg, Co, and Sr in the sediments indicate a source rock with a similar chemical composition as ba-salts. Müller and Stein (this volume) expect a source rock in the hinterland, which forms smectite by weathering to explain the high smectite contents in Ob Estuary's sediments. On the other hand in the catchment area of the Ob basaltic rocks are not exposed. Another explanation for these enrichments could be a fractionation due to water currents. Material with low density or small grain size would be transported into the outer Kara Sea, while heavier or larger minerals mainly accumulated in the estuaries. Thus, not only enrichments of Si, Zr and Ti could be explained, but also of Cr, which is incorporated in heavy minerals like chromite, for example. Co, Zn, and Pb could be enriched by scavenging with Fe- and Mn-oxyhydroxides (Murray, 1975). Ca and Sr are probably fixed in carbonates, which occur in benthic foraminifera, for example. However, Korsun (1998) studied onboard a sample from one site in the Yenisei estuary, which contained only a few soft-shelled allogromiids but no calcareous foraminifera. A more probable explanation could be that the source of particulate matter in the Ob River, the Quaternary sediments in Western Siberian Lowland, is depleted in orthoclase and richer in plagioclase. In this case Ca, Sr, and Na are enriched, K and Rb are depleted in comparison to an average shale.

Table 1: Mean element (El)/Al-ratios of surface sediments of the Ob and Yenisei estuaries as well as those of average shale (Taylor and McLennan, 1985) and of trapp basalts from the Putoran mountains (Lightfoot et al., 1990). Considered sites for the Yenisei Estuary are Men 4409, Men 4410, Men 4411, Men 4413, Men 4403, BP97-32, BP97-35, and BP97-39. Considered sites for the Ob Estuary are Men 4418, Men 4417, Men 4416, BP97-10, BP97-12, BP97-17, and BP97-47.

	Yenisei	Ob	Shale	Basalt
Ti/Al	0.08	0.07	0.06	0.08
Si/Al	3.53	4.42	2.93	2.62
Fe/Al	0.79	0.83	0.5	1
Mn/Al	0.03	0.044	0.009	0.016
Ca/Al	0.28	0.12	0.09	0.92
Mg/Al	0.27	0.18	0.13	0.48
K/Al	0.22	0.28	0.31	0.03
Na/Al	0.38	0.39	0.09	0.16
P/Al	0.014	0.021	0.007	0.005
Ba/Al [$\cdot 10^{-4}$]	51	62	65	n.d.
Co/Al [$\cdot 10^{-4}$]	3.5	3.2	2.3	5
Cr/Al [$\cdot 10^{-4}$]	15	14	11	20
Ni/Al [$\cdot 10^{-4}$]	7.6	5.9	5.5	11.4
Pb/Al [$\cdot 10^{-4}$]	2.2	3.2	2	n.d.
Rb/Al [$\cdot 10^{-4}$]	10	13	16	0.5
Sr/Al [$\cdot 10^{-4}$]	32	25	20	24
V/Al [$\cdot 10^{-4}$]	23	21	15	30
Y/Al [$\cdot 10^{-4}$]	3.4	3.9	2.7	2.6
Zn/Al [$\cdot 10^{-4}$]	13	12	8.5	12
Zr/Al [$\cdot 10^{-4}$]	22	32	21	11

Table 2. El/Al-ratios of some elements used for the formation of ferro-manganese nodules in surface sediments in the Western Kara Sea. Division of the Western Kara Sea into a northern and a southern province.

Northern part of Western Kara Sea				
Label core	Fe/Al	Mn/Al	Co/Al [$\cdot 10^{-4}$]	Ni/Al [$\cdot 10^{-4}$]
Men4380	0.79	0.15	4.6	7.4
Men4382	0.67	0.07	3	6.4
Men4386	0.84	0.07	3.7	6.3
Southern part of Western Kara Sea				
Label core	Fe/Al	Mn/Al	Co/Al [$\cdot 10^{-4}$]	Ni/Al [$\cdot 10^{-4}$]
Men4388	0.74	0.01	2.3	5.7
Men4391	0.71	0.01	2.3	5.6

The Western Kara Sea

Pavlov and Pfirman (1995) show the circulation pattern of surface water in the Kara Sea. Most of the water drained by the Yenisei River and some of the Ob River is transported by the Western Taymir Current into the Laptev Sea and the adjacent Arctic Ocean near Severnaja Zemlya. Another main direction for Ob River water is north to the continental margin and near the northern coast of Novaja Zemlya. There it is mixed with Arctic-Ocean-Barents-Sea-water and enters a gyre, which is cycling between Novaja Zemlya and Yamal Peninsula. In five investigated sites in the western Kara Sea the chemical composition varies slightly. The northern position is reduced in Rb and enhanced in Zr which is interpreted as a winnowing effect. The lighter material is probably transported by bottom currents. Therefore Rb is depleted and Zr enriched in the remaining sediment. Because of deep water renewal in the Novaja Zemlya Trough by the formation of ice and sinking of brines (Pavlov & Pfirman, 1995) deep water has to leave the trough in northern direction into the St. Anna Trough. This process probably causes higher current velocities at site Men 4382. At the other sites Zr/Al-ratios (Fig. 2) are lower and Rb/Al-ratios (Fig. 4) are higher, suggesting that bottom currents are weaker and sedimentation is less disturbed. Levitan (1995) divided the western Kara Sea into two provinces. In the southern part sedimentation rates surpass thoses in the northern part of this area. Thus, Mn/Al- and Ni/Al-ratios are increased in surface sediments of the northern three sites due to formation of ferromanganese nodules (Table 2), which needs a very low sedimentation rate (Halbach, 1986). The occurrence of ferromanganese micronodules in the northern province is confirmed by Levitan (1995).

Conclusions

Ob and Yenisei estuaries are different in their chemical composition of surface sediments. Yenisei Estuary sediments contain higher concentrations of elements which are enriched in basalts (e.g., Ni and Fe), and lower concentrations of elements which are depleted in basalts (e.g., Rb and Zr).

The "marginal filter" of both rivers are identified. Particulate matter as well as some dissolved and colloidal compounds precipitate in the Yenisei Estuary in an area around 73° N, in the Ob Estuary around 72° N.

Ferromanganese concretions occur in regions north of the Yenisei mouth and in northern part of the western Kara Sea as indicated by enhanced concentrations of Mn, Ni, and Fe.

Enhanced Zr/Al-ratios in context with low Rb/Al-ratios at site Men 4382 points to stronger bottom currents in northwards direction in the northern part of Novaja Zemlya Trough.

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Appendix 1: Element concentrations in surface sediments of the Ob and Yenisei estuaries and adjacent Kara Sea.

Latitude	Longitude	Station	Depth [m]	Al_2O_3 [%]	TiO_2 [%]	SiO_2 [%]	Fe_2O_3 [%]	MnO [%]	CaO [%]	MgO [%]	K_2O [%]	Na_2O [%]	P_2O_5 [%]
72.503	74.081	BP97-10	15	12.96	0.721	48.97	9.94	0.503	0.87	2.56	2.13	4.57	0.39
72.17	74.294	BP97-12	13	12.94	0.725	49.47	10.07	0.607	0.9	2.46	2.08	4.14	0.412
72.689	73.731	BP97-17	20	11.48	0.712	57.47	7.28	0.388	1.11	2.04	2.1	4.67	0.295
74.001	79.025	BP97-19	30	12.41	0.708	47.31	9.16	0.422	1.48	3.07	2.15	6.07	0.366
74.001	81.008	BP97-21	41	12.43	0.729	51.75	7.98	0.421	1.56	2.99	2.14	5.53	0.25
74.089	80.093	BP97-27	19	13.06	0.802	45.81	8.88	0.919	1.82	3.58	1.98	6.29	0.282
72.093	81.481	BP97-32	10	13.89	0.926	50.4	8.78	0.274	2.43	3.6	1.83	3.7	0.25
72.509	80.329	BP97-35	14	14.13	0.961	53.24	8.75	0.377	2.52	3.44	1.92	3.22	0.268
73.536	79.918	BP97-39	40	11.41	0.749	57.37	7.19	0.478	1.9	2.81	1.97	4.72	0.227
73.899	81.667	BP97-42	32	9.93	0.786	65.7	5.41	0.241	2.01	2.19	1.93	3.7	0.153
73.999	77.204	BP97-46	27	11.62	0.685	50.21	7.87	0.561	1.32	2.78	2.11	6.39	0.296
72.584	73.749	BP97-47	18	11.49	0.735	58.38	6.94	0.477	1.26	1.98	2.09	4.77	0.275
72.961	73.148	BP97-48	29	10.74	0.703	61.22	6.27	0.359	1.22	1.87	2.14	4.63	0.239
73.21	72.895	BP97-49	29	11.01	0.701	56.59	6.71	0.358	1.43	2.11	2.12	5.46	0.263
73.611	72.951	BP97-50	28	10.88	0.686	57.96	6.56	0.434	1.15	2.1	2.14	5.16	0.243
74	72.662	BP97-52	30	10.05	0.618	67.29	4.69	0.199	1.2	1.49	2.26	3.76	0.177
73.224	75.619	BP97-55	14	12.34	0.767	57.89	7.7	0.61	1.42	2.26	2.15	3.48	0.276
72.89	75.483	BP97-56	14	11.07	0.772	63.57	5.84	0.414	2.13	1.78	2.12	3.05	0.214
73.65	74.839	BP97-58	23	9.16	0.627	68.83	4.67	0.278	1.32	1.47	2.13	3.44	0.193
72.637	59.972	Men4380	87	12.76	0.68	58.44	7.65	1.28	1.11	2.35	2.64	3.96	0.36
74.561	63.005	Men4382	87	12.08	0.74	64.67	6.12	0.58	1.16	1.68	2.49	3.37	0.21
72.692	64.565	Men4386	75	12.35	0.73	60.4	7.81	0.55	1.09	2.04	2.53	3.81	0.33
71.019	64.621	Men4388	70	14.04	0.85	57.71	7.86	0.13	0.96	2.35	2.62	3.91	0.34
69.777	64.863	Men4391	46	13.39	0.81	58.36	7.22	0.13	1.45	2.43	2.64	3.99	0.32
74.988	79.852	Men4399	42	13.72	0.76	52.01	9.19	2.4	1.01	2.59	2.62	4.69	0.3
74.004	79.955	Men4401	33	13.77	0.78	52.8	9.52	0.54	1.47	2.83	2.45	4.46	0.34
73.003	79.93	Men4403	25	14.68	0.86	49.68	9.82	0.48	1.8	3.55	2.41	4.79	0.32
71.314	82.982	Men4409	22	14.44	1.03	56.05	8.43	0.21	3.92	3.49	1.73	2.88	0.23
71.605	83.319	Men4410	21	13.45	0.99	58.21	7.34	0.1	3.46	3.11	1.9	3.25	0.18
71.822	82.642	Men4411	29	13.99	0.97	55.87	8.02	0.14	3.36	3.3	1.87	3.66	0.22
72.218	81.449	Men4413	13	14.35	1.01	56.95	7.6	0.16	3.44	3.21	1.91	3.69	0.22
73.651	73.517	Men4414	26	12.64	0.76	61.21	7.78	0.2	1.15	2.01	2.39	3.73	0.31
71.743	73.088	Men4416	19	13.38	0.79	57.86	9.42	0.42	1.08	2.2	2.26	2.95	0.38
70.915	73.502	Men4417	20	9.89	0.7	74.97	4.14	0.06	0.93	1.15	2.1	1.72	0.13
68.824	73.611	Men4418	14	12.81	0.85	69.48	6.02	0.16	1.37	1.39	2.13	1.78	0.28

Appendix 1 (continued)

Station	As [ppm]	Ba [ppm]	Co [ppm]	Cr [ppm]	Ni [ppm]	Pb [ppm]	Rb [ppm]	Sr [ppm]	V [ppm]	Y [ppm]	Zn [ppm]	Zr [ppm]
BP97-10	36	319	23	98	46	20	101	149	167	28	94	132
BP97-12	32	341	28	98	46	22	97	149	163	28	96	133
BP97-17	32	389	19	86	31	17	85	178	134	25	71	199
BP97-19	49	310	25	94	47	16	89	174	211	26	91	129
BP97-21	34	343	24	101	47	13	86	180	188	24	88	147
BP97-27	26	300	29	103	60	14	86	206	184	26	102	118
BP97-32	12	336	30	111	62	12	80	230	175	27	111	137
BP97-35	17	342	29	109	60	14	81	231	186	29	104	151
BP97-39	26	348	21	109	39	15	77	192	169	23	77	176
BP97-42	17	413	18	108	29	11	68	191	136	21	56	351
BP97-46	40	331	24	95	39	15	86	178	187	25	80	159
BP97-47	25	405	20	90	32	16	82	187	128	24	67	189
BP97-48	30	423	17	89	27	16	82	184	133	24	59	256
BP97-49	36	378	19	84	29	15	83	188	143	24	66	217
BP97-50	37	393	20	88	29	15	84	172	156	23	65	213
BP97-52	27	479	15	71	22	13	75	184	115	22	46	242
BP97-55	32	399	22	92	37	17	85	192	160	28	78	193
BP97-56	21	446	17	96	31	15	79	225	120	25	59	301
BP97-58	25	466	15	76	20	14	73	181	103	20	44	329
Men4380	49	471	31	103	50	20	90	171	179	19	87	157
Men4382	41	392	19	103	41	21	81	187	179	21	83	230
Men4386	71	456	24	89	41	19	86	168	202	22	82	185
Men4388	72	415	17	116	42	21	100	145	196	23	98	165
Men4391	50	414	16	103	40	22	91	190	179	21	88	169
Men4399	59	452	28	103	54	24	95	189	224	22	104	153
Men4401	46	311	21	103	45	22	83	166	185	23	91	145
Men4403	27	357	25	116	60	21	84	186	196	24	108	130
Men4409	13	412	32	116	59	15	58	276	157	23	99	171
Men4410	10	405	24	123	52	17	60	256	157	24	91	201
Men4411	10	378	23	116	57	19	61	258	134	24	95	161
Men4413	12	390	24	82	54	16	63	264	146	25	92	166
Men4414	43	426	17	89	35	20	83	170	140	24	75	177
Men4416	27	421	23	96	42	26	84	160	129	24	85	164
Men4417	12	436	14	82	33	16	70	142	106	20	62	310
Men4418	13	424	18	96	37	28	77	169	95	24	77	251

MICROPALEONTOLOGY

NEW DATA ON DIATOM DISTRIBUTION IN SURFACE SEDIMENTS OF THE KARA SEA

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Abstract

Diatom abundance and composition of assemblages have been determined in 20 sediment samples from Ob' and Yenisei estuaries and the adjacent Kara Sea shelf areas. Taxonomically diverse (169 species and varieties) and abundant (total sum - up to 71.5 million valves/g dry sediment) diatom assemblages were recorded in all studied sediment samples. The maximum diatom abundance in the sediments observed in the Ob (up to 54.7 million valves/g) and Yenisei (up to 71.5 million valves/g) estuaries, and predominance of fresh-water riverine species (up to 98.4%) gives evidence for allochtonous origin of organic matter in estuaries. Surface sediments of the inner Kara shelf adjacent to the river estuaries are characterized by high abundance of diatoms as compared with the other studied regions of the Kara Sea, with predominance of marine (up to 85.9%), mainly planktonic (up to 66.4%) and sea-ice (up to 81.7%) species indicating river-induced production due to nutrient influx.

Introduction

Studies on the diatom flora of the Kara Sea have been carried out since the nineties of the 19th century (Cleve, 1883; Meunier, 1910; Kisselev, 1935; Shirshov, 1937; Zabelina, 1931; Khmyznikova and Zabelina, 1946; Usachev, 1946, 1968; Il'yash and Koltsova, 1981; Kol'tsova Il'yash, 1982; Bondarchuk et al., 1985). However, practically all these investigations were devoted to planktonic and sea-ice diatom floras of the Kara Sea including its taxonomic composition, seasonal changes of species and successions, and quantitative characteristics of phytocoenoses. Some aspects have been emphasized in these studies: (i) distribution patterns of diatoms in the Kara Sea reflect the origin of water masses and their circulation in this basin; (ii) the south-eastern part of the sea influenced by intensive river runoff is characterized by diversity of phytocoenotic groups dominated by freshwater diatoms typical of the Yenisei and Ob' plankton; (iii) in the south-western part of the sea freshened by the Pechora Sea waters euryhaline species are most abundant; (iiii) - neritic arctic-boreal and sea-ice species predominate in the central and northern parts of the sea (transect from Zhelaniya cape to Severnaya Zemlya).

By now the total list of planktonic diatoms of the Kara Sea includes more than 80 taxa (Polyakova, 1988). Biogeographical composition of the diatom flora is rather uniform: arctic-boreal species - 41%, bipolar - 7%, cosmopolitan - 26%, arctic-boreal-tropic - 12%, species of unknown phytogeographical characteristic - 14%. Predominance of cold water marine diatom assemblages with arctic-boreal and bipolar species (total 48%) indicate predominance of arctic water masses in the Kara Sea. At the same time, relatively high abundances of species with wide geographical range (cosmopolitan and arctic-boreal-tropic ones, total 38%) gives evidence for diverse abiotic conditions in the Kara Sea depending upon intensive river runoff and influence of transformed Barents Sea waters on hydrobiological conditions in the western sector of the sea.

Diatoms are known to indicate paleoenvironmental conditions. However, there has been surprisingly little work done on the distribution and oceanographic significance of species in the surface sediments of the Kara Sea (Cleve and Grunow, 1880; Cleve, 1883). A previous author's study (Polyakova, 1997) revealed very scarce occurrences of modern diatoms in sediments of the western and north-western Kara Sea. The purpose of this paper is to analyse diatom distribution in surface sediments of the southernmost part of the Kara Sea (Fig. 1). This region including the Ob' and Yenisei estuaries and the adjacent Kara Sea shelf are most sensitive and important areas for understanding the interaction between sea and river waters in the Eurasian Arctic.

Material and Methods

The surface sediment samples were collected during the Joint Russian-German Expedition during the 28th cruise of the RV "Akademik Boris Petrov" to the Kara Sea, Ob' and Yenisei estuaries in August-October 1997 (Matthiessen and Stepanets, 1998). This study deals with analysis of twenty sediment samples (Table 1, Fig. 1). All surface samples were collected from the 0-1 cm intervals of multi corer cores.

Table 1. Geographic positions of the studied surface sediment samples from the Kara Sea.

Station No.	Latitude	Longitude	Water Depth (m)
BP 97-10	72°30'10.0"	74°04'51.0"	15
BP 97-12	72°10'13.0"	74°17'37.0"	13
BP 97-17	72°41'19.2"	73°43'50.4"	20
BP 97-19	74°00'02.4"	79°01'28.4"	30
BP 97-21	74°00'02.4"	81°00'27.6"	41
BP 97-27	72°53'21.0"	80°05'33.0"	19
BP 97-32	72°05'35.4"	81°28'52.2"	10
BP 97-35	72°30'31.2"	80°19'43.2"	14
BP 97-39	73°32'09.6"	79°55'03.0"	40
BP 97-42	73°53'57.6"	81°40'01.2"	32
BP 97-43	73°42'33.0"	82°48'48.0"	31
BP 97-46	73°59'57.6"	77°12'14.4"	27
BP 97-47	72°35"00.6"	73°44'54.6"	18
BP 97-48	72°57'40.8"	73°08'51.6"	29
BP 97-49	73°12'34.2"	72°53'40.8"	29
BP 97-50	73°36'39.6"	72°57'04.8"	28
BP 97-52	74°00'01.2"	72°39'42.2"	30
BP 97-55	73°13'27.9"	75°37'08.4"	14
BP 97-56	72°53'23.4"	75°28'57.0"	14
BP 97-58	73°39'01.2"	74°50'19.2"	23

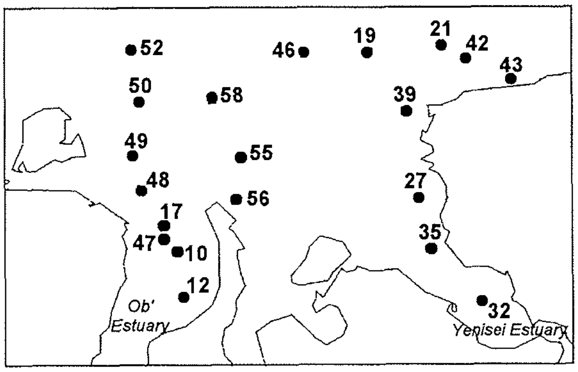

Fig. 1. Station map with investigated surface sediment samples.

The following methods were used for preparation of diatom slides and determination of absolute diatom abundance per gram of dry sediment. Diatoms were concentrated by treatment with 10% HCl, and with 30% H_2O_2, with subsequent decantation with distilled water. Subsequently the residues were mounted on glass slides using a mounting medium having a high index of refraction (1.68). The valves were examined under a light microscope at x1000 magnification. The first 300-400 specimens encountered in each sample were identified, and their abundance was converted to percent and number of valves per gram of dry sediment. The complete floral list is given in Appendix 1.

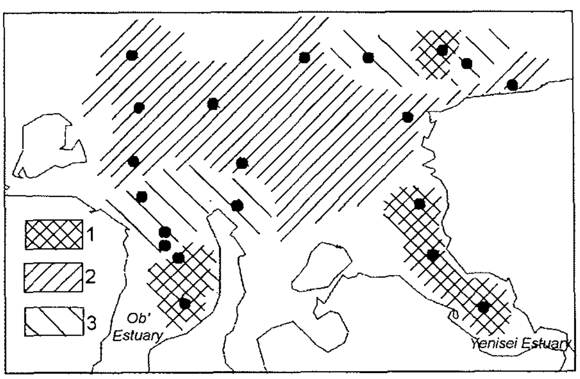

Fig. 2. Distribution of diatom valves/g dry sediment in surface sediments from the Kara Sea (Mio. valves/g: 1 -> 5; 2 - 3-5; 3 - <3).

Results

The list of diatoms found in the surface sediment samples of the studied area of the Kara Sea is given in Appendix 1. In total 169 species and varieties have been identified, including 58 marine and brackish water - marine, and 111 freshwater species. The taxonomically most diverse genus is *Navicula* (25 taxa); the genera *Thalassiosira* (12 taxa), *Nitzschia* (11 taxa), *Gomphonema* (9 taxa), *Pinnularia* (9 taxa), *Eunotia* (8 taxa) and *Aulacoseira* (6 taxa) being also diverse. Marine and brackish water-marine diatoms are represented by planktonic (mainly neritic taxa, 25), sublittoral benthic and semi-benthic (33 taxa), and sea-ice (7 taxa) species. Freshwater diatoms are represented by planktonic (14 taxa) and benthic and periphytic (111 taxa) species.

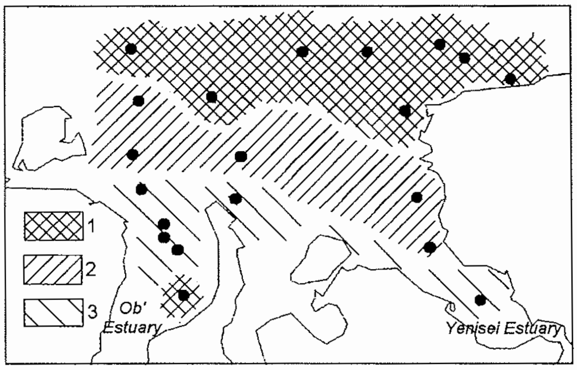

Fig. 3. Distribution of *Nitzschia grunowii* + *N. cylindrus* + *Fossula arctica* in surface sediments from the Kara Sea (Mio. valves/g: 1 ->0.5; 2 - 0.1 - 0.5; 3 - <0.1).

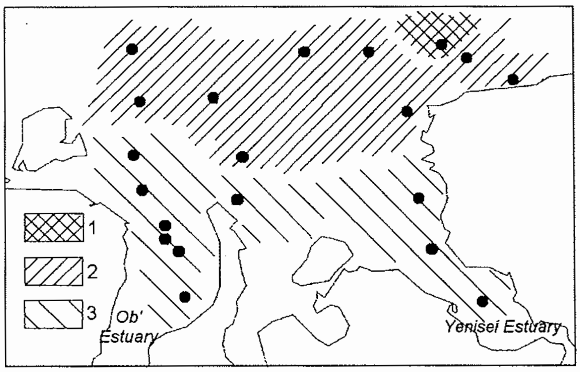

Fig. 4. Distribution of *Thalassiosira antarctica* + *T. gravida* in surface sediments from the Kara Sea (Mio. valves/g: 1 ->0.5; 2 - 0.1 - 0.5; 3 - <0.1).

The total diatom abundance in all studied samples is high ranging from 1.0 to 71.5 million valves per gram of dry sediment (Fig. 2). The total abundance of marine diatoms reaches 17.8 million valves/g, and that of freshwater ones - 65.7 million valves/g. Sea-ice species (up to 14.7 million valves/g) together with planktonic, mainly neritic species (up to 16.9 million valves/g) are most abundant among marine diatoms. Marine sublittoral species are not abundant (up to 0.5 million valves/g). Their share in diatom assemblages ranges from 0.3 to 15.9%.

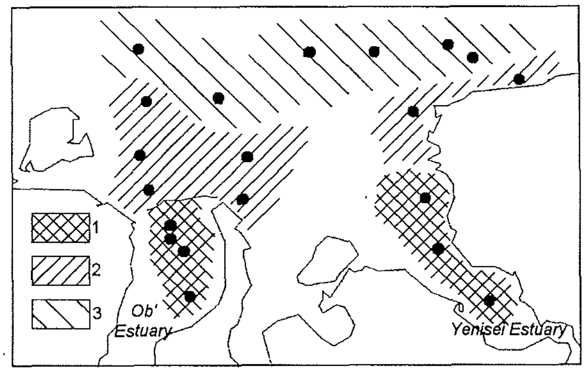

Fig. 5. Distribution of freshwater diatoms in surface sediments from the Kara Sea (1- >80; 2 - 50 - 80; 3- < 50%).

The species group *Nitzschia grunowii+N. cylindrus+Fossula arctica* with the total abundance of 13.8 million valves/g dominates among sea-ice species (Fig. 3) *Thalassiosira antarctica+T. gravida* (up to 0.7 million valves/g, Fig. 4) and *T. nordenskioeldii* (up to 1.1 million valves/g) are most abundant among marine planktonic diatoms. Planktonic species of the genus *Aulacoseira* (Appendix 1) predominate among freshwater diatoms (up to 45.1 million valves/g, Figs. 5,6). Planktonic freshwater species belonging to the genus *Stephanodiscus* are also abundant (9.6 million valves/g).

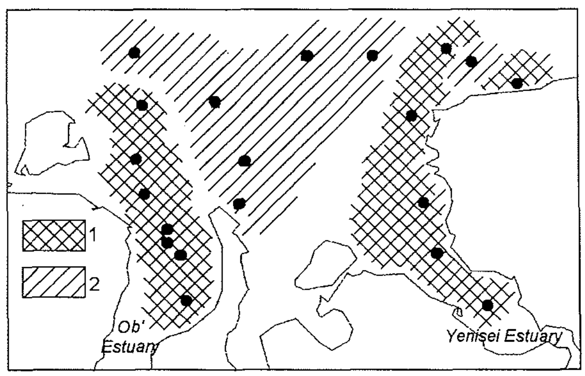

Fig. 6. Distribution of *Aulacoseira* species valves in surfave sediments from the Kara Sea (Mio. valves/g: 1 ->1; 2 - <0.1).

Besides modern diatoms, the Kara Sea surface sediment samples contain rare redeposited poorly preserved valves of marine Paleogene diatoms of *Gladius*, *Hemiaulus*, *Pyxidicula*, and other genera.

Discussion

The distribution patterns of diatoms in the surface sediments of the Ob' and Yenisei estuaries and the adjacent inner shelf of the Kara Sea raised some questions concerning (i) the origin of organic matter in the sediments of this area, (ii) productivity in the frontal zone, and (iii) the influence of river runoff on the hydrographic and biological regimes in the shelf zones and its biota.

Extremely high diatom abundance in the sediments (Fig. 2) is the most striking feature of diatom assemblages, especially if compared with the scarce occurrence of modern diatoms in the previously studied western and north-western regions of the Kara Sea (Polyakova, 1997). It is known, that the bulk of nutrients introduced by rivers is taken up by diatom productivity in the coastal areas (e.g. Abrantes, 1990). The maximum diatom abundances has been observed in the Ob' (up to 54.7 million valves/g) and Yenisei (up to 71.5 million valves/g) estuaries. Concentration of diatom valves generally decreases offshore from the estuaries to the inner shelf, thus being in good accordance with opal distribution patterns in the Kara Sea surface sediments (Nürnberg, 1996).

The investigation area may be subdivided into two sedimentary provinces corresponding to (1) river estuaries and (2) inner shelf according to the composition of diatom assemblages. In the river estuaries, notwithstanding strongly changing salinity conditions from almost fresh to brackish ones, freshwater species are dominant (Fig. 5) - up to 98.4% in Ob' Estuary, and - up to 95.9% in the Yenisei Estuary. Riverine planktonic species of the genera *Aulacoseira* and *Stephanodiscus* are the dominant species in the estuaries with total abundance of 45.1 million valves/g (Fig. 6) and 9.6 million valves/g, respectively.

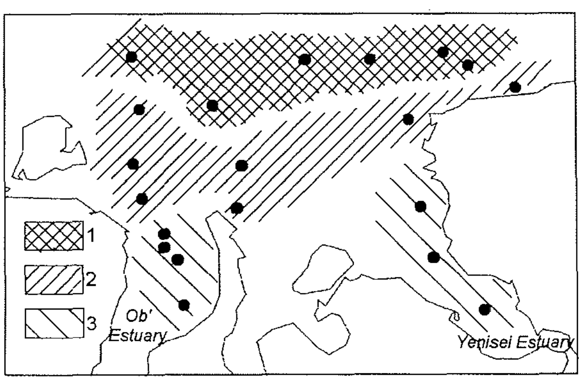

Fig. 7. Distribution of marine and brackish water diatoms in surface sediments from the Kara Sea (1 ->50; 2 - 10-50; 3 -<10%).

Marine and brackish water species are mainly represented by euryhaline species (*Thalassiosira baltica, Melosira moniliformis* and others) and rare planktonic neritic and sea-ice species. Their occurrence in the Ob' and Yenisei estuaries (7.7% and 6.6%, respectively, Fig. 7) is evidence of sea water influx from the Kara Sea. Thus, in this region organic matter is probably of allochtonous origin, and its higher opal contents in sediments may be related to higher sedimentation rates for fine material and associated higher fluxes of allochtonous diatoms to the sediments, as has been previously supposed on the basis of preliminary sedimentological investigations (Matthiessen et al., 1998).

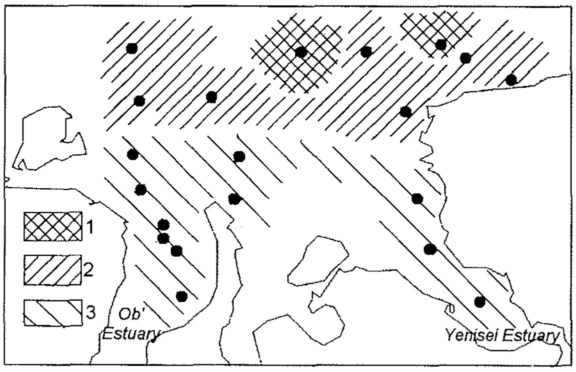

Fig. 8. Distribution of sea-ice diatoms in surface sediments from the Kara Sea (1 ->50; 2 - 10-50; 3 -<10%).

The second sedimentary province corresponds to the inner Kara shelf adjacent to the river estuaries. On the whole, diatom abundance here is lower than in the Ob' and Yenisei estuaries ranging from 1.0 to 4.7 million valves/g with local extremely high abundances (24.4 million valves/g, Fig. 2) in the north-eastern part of the investigation area. This is considerably higher than in other regions of the central and western Eurasian shelf (Polyakova, 1997). Marine diatoms dominate assemblages in all studied shelf sediment samples (up to 85.9%). Sea-ice and marine planktonic forms characteristic for the region are the most abundant groups (up to 66.4% and 81.7% respectively, and up to 14.7 and 16.9 million valves/g, Figs. 8, 9). This indicates that marine production contributes significant amounts to organic matter in this region as has been previously suggested (Matthiessen et al., 1998). High primary productivity in some localities of the open sea might be induced by nutrient influx from the rivers.

One of the major scientific questions was a possible change in composition of diatom assemblages along the salinity gradient. The gradual decrease in abundance and percentage of freshwater diatoms in sediments offshore the Ob' and Yenisei estuaries (Fig. 5) is obviously related to the gradual increase of surface water salinity. Correspondingly, percentage and taxonomic diversity of marine diatoms increases (Fig. 7), mainly due to planktonic neritic and panthalassic (Fig. 9) and sea-ice species (Fig. 8). The sharpest change occurred along the transects at 73°30'N. It is likely that this boundary corresponds to the average multi-annual position of the frontal zone in the outer part of the Ob' and Yenisei estuaries.

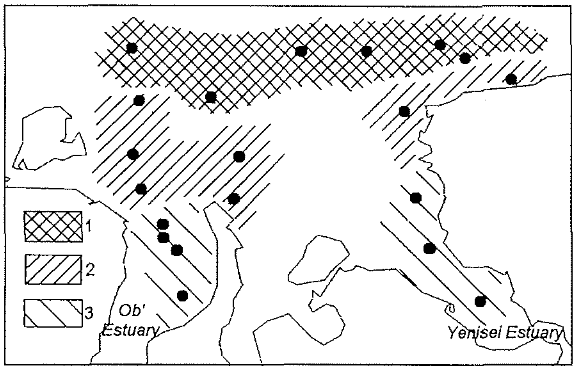

Fig. 9. Distribution of marine planktonic diatoms in surface sediments from the Kara Sea (1 ->50; 2 - 10-50; 3 -<10%).

Taxonomic composition of marine planktonic diatoms in the investigation area only slightly reflects (25%) the total diversity of diatom flora in the Kara Sea (Polyakova, 1988). The main reduction in taxonomic diversity is caused by species of the genus *Chaetoceros* which are dominant in phytoplankton of several Kara Sea regions. Only two species (*C. septentrionalis*, *C. mitra*) among 23 phytoplanktonic ones have been found in the sediments. Additionally, rare and non-abundant species of, for instance, the genera *Coscinodiscus* and *Rhizosolenia*, have not been reported. At the same time, distribution of dominant planktonic and sea-ice diatom species generally follows their modern distribution patterns.

Conclusions

1) Taxonomically diverse (169 species and varieties) and abundant (total sum - up to 71.5 million valves/g dry sediment) diatom assemblages have been recorded in surface sediments of the Ob' and Yenisei estuaries and the adjacent Kara Sea shelf.

2) The maximum diatom abundance in the sediments in the Ob' (up to 54.7 million valves/g) and Yenisei (up to 71.5 million valves/g) estuaries, and predominance of freshwater riverine species (up to 98.4%) gives evidence for an allochtonous origin of organic matter and opal in the estuaries.

3) Surface sediments of the inner Kara shelf adjacent to the river estuaries are characterized by high abundance of diatoms as compared with the other studied regions of the Kara Sea, with predominance of marine (up to 85.9%)

mainly planktonic (up to 66.4%) and sea-ice (up to 81.7%) species indicating river-induced production due to nutrient influx.

4) Freshwater diatoms gradually decrease in abundance and percentages in sediments offshore off the Ob' and Yenisei estuaries, associated with the monotonous increase of surface water salinity. The sharpest changes observed along the transects at 73°30'N correspond possibly to the average multi-annual position of the frontal zone in the outer part of the Ob' and Yenisei estuaries.

Acknowledgements

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Appendix 1. List of diatom species present in the studied surface sediment samples of the Kara Sea.

Diatom species	Ecoloy
Amphiprora kjellmanii Cl.	m-pl
Amphora coffeaformis Agardh	m-sub
Amphora costata Smith	m-sub
Amphora ovalis Kütz.	m-sub
Bacterosira concava-convexa Makarova	m-pl
Bacterosira fragilis Gran	m-pl
Caloneis aemula Schmidt	m-sub
Chaetoceros mitra (Bail.)Cl.	m-pl
Chaetoceros septentrionalis Oestr.	m-pl
Chaetoceros spp.	m-pl
Cocconeis scutellum Ehr.	m-sub
Coscinodiscus oculus-iridis Ehr.	m-pl
Diploneis smithii (Breb.)Cl.	m-sub
Diploneis smithii var. *pumila* (Grun.)Hust.	m-sub
Diploneis smithii f. *rhombica* Mereschkowsky	m-sub
Diploneis subcincta (Schmidt)Cl.	m-sub
Diploneis suborbicularis (Greg.)Cl.	m-sub
Fallacia forcipata (Grev.)Stichle et Mann	m-sub
Fossula arctica Hasle, Syvertsen et Quillfeld	m-pl,s-i
Melosira juergensii Agardh	m-sub
Melosira moniliformis (Müller) Agardh	m-sub
Navicula cancellata Donk	m-sub
Navicula distans Smith	m-sub
Navicula gregaria Donk.	m-sub
Navicula latissima Greg.	m-sub
Navicula superba Cl.	m-sub
Navicula transitans Cl.	m-sub,s-i
Navicula transitans var. *derasa* Grun.	m-sub
Navicula valida Cl.	m-sub
Navicula vanhoeffenii Gran	m-pl,s-i
Navicula sp.	m-sub
Nitzschia cylindrus (Grun.) Hasle	m-pl,s-i
Nitzschia frigida Grun.	m-sub
Nitzschia grunowii Hasle	m-pl,s-i
Nitzschia laevissima Grun.	m-sub
Nitzschia obtusa var. *kryophila* Cl.	m-sub
Nitzschia polaris Grun.	m-pl,s-i
Paralia sulcata (Ehr.) Cl.	m-sub
Pinnularia quadratarea Schmidt.	m-sub
Pinnularia quadratarea var. *baltica* Grun.	m-sub
Plagiogramma staurophorum (Greg.) Heib.	m-sub
Porosira glacialis (Grun.)Jörg.	m-pl
Pseudogomphonema arctica Grun.	m-sub,s-i
Pseudogomphonema groenlandicum Oestr.	m-sub
Synedra tabulata (Agardh) Kütz.	m-sub
Thalassionema nitzschioides Grun.	m-pl
Thalassiosira anguste-lineata (Schmidt) Fryx.et Hasle	m-pl
Thalassiosira antarctica Comber	m-pl
Thalassiosira baltica (Grun.) Ostenfeld	m-pl
Thalassiosira bioculata (Grun.) Ostenfeld	m-pl
Thalassiosira constricta Gaarder	m-pl
Thalassiosira gravida Cl.	m-pl
Thalassiosira hyalina (Grun.) Gran	m-pl
Thalassiosira hyperboreae (Grun.) Hasle et Lange	m-sub
Thalassiosira incerta Makarova	m-pl
Thalassiosira nordenskioeldii Cl.	m-pl
Thalassiosira rotula Meunier	m-pl
Thalassiosira sp.1	m-pl

Appendix 1 cont'd. List of diatom species present in the studied surface sediment samples of the Kara Sea.

Diatom species	Ecology
Achnanthes conspicua Kütz.	fr-b
Achnanthes delicatula (Kütz.) Grun.	fr-b
Achnanthes fragilarioides Boye P.	fr-b
Achnanthes hauckiana Grun.	fr-b
Achnanthes linearis (Smith) Grun.	fr-b
Achnanthes minutissima Kütz.	fr-b
Asterionella formosa Hassal	fr-pl
Aulacoseira distans (Ehr.) Simonsen	fr-pl
Aulacoseira granulata (Ehr.) Simonsen	fr-pl
Aulacoseira islandica (Müller) Simonsen	fr-pl
Aulacoseira italica (Ehr.) Simonsen	fr-pl
Aulacoseira italica var. *tenuissima* (Grun.) Simonsen	fr-pl
Aulacoseira subarctica (Müller) Haworth	fr-pl
Caloneis silicula (Ehr.) Cl.	fr-b
Cocconeis placentula Ehr. et var. *intermedia* (Herib.et Perag.) Cl.	fr-b
Cyclotella comta (Ehr.) Kütz.	fr-pl
Cyclotella comta var. *oligactis* (Ehr.) Grun.	fr-pl
Cyclotella kützingiana Thwaites	fr-pl
Cyclotella meneghiniana Kütz.	fr-pl
Cyclotella ocellata Pant.	fr-pl
Cymatopleura solea (Breb.) Smith	fr-b
Cymbella affinis Kütz.	fr-b
Cymbella cistula (Ehr.) Kirchner	fr-b
Cymbella cymbiformis Agardh	fr-b
Cymbella sinuata Greg.	fr-b
Cymbella ventricosa Kütz.	fr-b
Diatoma hiemalis (Roth) Heiberg	fr-b
Diatoma vulgaris Bory	fr-b
Didymosphenia geminata (Lyngbye)Schmidt	fr-b
Epithemia zebra (Ehr.)Kütz.et var. *porcellus* (Kütz.)Grun. et var. *longicornis* Grun.	fr-b
Epithemia zebra var. *porcellus* (Kütz.)Grun.	fr-b
Epithemia zebra var. *longicornis* Grun.	fr-b
Eunotia diodon Ehr.	fr-b
Eunotia faba (Ehr.) Grun.	fr-b
Eunotia fallax Cleve-Euler	fr-b
Eunotia parallela Ehr.	fr-b
Eunotia polydentula Brunth.	fr-b
Eunotia praerupta Ehr.et var. *bidens*	fr-b
Eunotia praerupta var. *bidens* Smith	fr-b
Eunotia septentrionalis Oestr.	fr-b
Fragilaria arcus (Ehr.)Cl.	fr-b
Fragilaria capucina Desmazieres	fr-b
Fragilaria constricta Ehr.	fr-b
Fragilaria construens (Ehr.)Hust.	fr-b
Fragilaria construens var. *binodis* (Ehr.) Hust.	fr-b
Fragilaria inflata (Heib.) Hust.	fr-b
Fragilaria leptostauron (Ehr.) Hust.	fr-b
Fragilaria pinnata Ehr.	fr-b
Fragilaria ulna (Nitzsch) Lange-Bertalot	fr-b
Fragilaria virescens Ralfs	fr-b
Fragilaria virescens var. *capitata* Oestr.	fr-b
Frustulia rhomboides (Ehr.) De Toni	fr-b
Gomphonema acuminatum Ehr.	fr-b
Gomphonema acuminatum var. *brebissonii* (Kütz.) Cl.	fr-b
Gomphonema intricatum Kütz.	fr-b
Gomphonema intricatum var. *pumila* Grun.	fr-b
Gomphonema lanceolatum Ehr.	fr-b
Gomphonema longiceps Ehr.	fr-b
Gomphonema longiceps var. *subclavata* Grun.	fr-b
Gomphonema quadripunctatum (Oestr.) Wislouch	fr-b

Appendix 1cont.´d. List of diatom species present in the studied surface sediment samples of the Kara Sea.

Diatom species	Ecology
Hantzschia amphioxis (Ehr.) Grun.	fr-b
Meridion circulare (Grev.) Agardh	fr-b
Navicula cincta (Ehr.) Kütz.	fr-b
Navicula contenta Grun.	fr-b
Navicula costulata Grun.	fr-b
Navicula cryptocephala Kütz.	fr-b
Navicula cryptocephala Kütz. et var. *lata* Poretzky et Anissimova	fr-b
Navicula dicephala (Ehr.)Smith	fr-b
Navicula gracilis Ehr.	fr-b
Navicula mutica Kütz.	fr-b
Navicula placentula var. *rostrata* A.Mayer	fr-b
Navicula pupula Kütz.	fr-b
Navicula pupula var. *capitata* Hust.	fr-b
Navicula radiosa Kütz.	fr-b
Navicula rhynchocephala Kütz.	fr-b
Navicula seminulum Grun.	fr-b
Navicula viridula Kütz.	fr-b
Neidium affine (Ehr.) Cl.	fr-b
Neidium bisulcatum (Langerstedt) Cl.	fr-b
Nitzschia bremensis Hust.	fr-b
Nitzschia palea (Kütz.) Smith.	fr-b
Nitzschia palea var. *debilis* (Kütz.) Grun.	fr-b
Nitzschia tryblionella Hantzsch	fr-b
Nitzschia tryblionella var. *ambiqua* Grun.	fr-b
Pinnularia borealis Ehr.	fr-b
Pinnularia brevicostata Cl.	fr-b
Pinnularia leptosoma f. *robusta* Schirschow	fr-b
Pinnularia major (Kütz.) Cl.	fr-b
Pinnularia microstauron (Ehr.) Cl.	fr-b
Pinnularia microstauron var. *brebissonii* f. *deminuta* Grun.	fr-b
Pinnularia subborealis Hust.	fr-b
Pinnularia viridis (Nitzsch) Ehr.	fr-b
Pinnularia viridis var. *fallax* Cl.	fr-b
Rhoicosphenia curvata (Kütz.) Grun.	fr-b
Rhopalodia gibba (Ehr.) Müller	fr-b
Stauroneis anceps Ehr.	fr-b
Stauroneis parvula var. *prominula* Grun.	fr-b
Stauroneis phoenicenteron (Nitzsch) Ehr.	fr-b
Stauroneis smithii Grun.	fr-b
Stephanodiscus astraea var. *intermedia* Fricke	fr-pl
Stephanodiscus huntzschii Grun.	fr-pl
Surirella angustata Kütz.	fr-b
Surirella ovata Kütz. et var. *salina*	fr-b
Surirella ovata var. *salina* Smith	fr-b
Synedra goulardii var. *telezkoensis* Poretzky	fr-b
Synedra vaucheriae Kütz.	fr-b
Tabellaria fenestrata (Lyngbye) Kütz.	fr-b
Tabellaria flocculosa (Roth) Kütz.	fr-b
Tetracyclus emarginatus (Ehr.) Smith	fr-b
Tetracyclus rupestris (Braun) Grun.	fr-b

Key:

m - marine and brackish water species, fr - freshwater species, p - planktonic and panthalassic species, sub - sublittoral benthic and semi-benthic species, s-i - sea-ice species, b - benthic and periphytonic species.

DISTRIBUTION OF PALYNOMORPHS IN SURFACE SEDIMENTS FROM THE OB AND YENISEI ESTUARIES (KARA SEA, ARCTIC OCEAN)

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Introduction

The inner Kara Sea is a marine environment which is strongly influenced by seasonally variable freshwater discharge by the rivers Ob and Yenisei. Due to extensive supply of continental sediments with the riverine water, marine organic matter may significantly be diluted with freshwater and terrestrial organic matter. Organic geochemical and biomarker analyses previously revealed that the bulk of organic matter in surface sediments from the Kara Sea and in particular from the estuaries of Ob and Yenisei has a terrestrial source (Stein, 1996; Belayeva and Eglington, 1997). Detailed geochemical, biomarker and maceral analyses of the surface sediments collected in the Ob and Yenisei bays on the expedition with RV "Akademik Boris Petrov" in 1997 confirmed that marine organic matter contributes only small but offshore increasing amounts (Boucsein et al., this volume). The different sources of aquatic organic matter, however, can not always be characterized because freshwater, brackish water and marine organisms may have a similar biogeochemical composition (e.g. Fahl and Stein, 1998).

Palynological investigations on fossilizable particulate organic matter may help to overcome some obstacles of geochemical investigations. Traditionally, exclusively pollen are considered in palynology. In the past years, the potential of other organic-walled microfossils frequently associated with pollen in samples from aquatic environments has been recognized to determine biological origin, source and age of organic matter. Palynomorphs are now considered a diverse group of particles of biological origin from aquatic and terrestrial environments which may be studied with light microscope techniques. Terrestrial palynomorphs comprise pollen, spores, leaf cuticules, wood fragments, charcoal etc., while aquatic palynomorphs consist of tests and cysts of phyto- and zooplankton (e.g. dinoflagellates, dinoflagellate cysts, prasinophytes, chlorococcalean algae, cladocerans, tintinnids) and zoobenthos (e.g. benthic foraminifer). Additionally, organisms of unknown biological affinity which produce fossilizable organic-walled hard parts may be found. These acritarchs may be as abundant as other groups of palynomorphs in shelf environments (e.g. Mudie, 1992; Kunz-Pirrung, 1998, in press).

Therefore, the aquatic portion of organic matter (particles larger than 6μm) may be characterized by palynological methods. In this paper the major trends in aquatic palynomorph distribution in relation to the salinity gradient in the Ob and Yenisei estuaries are described. The distribution of acritarchs is not shown because their biological affinity is unknown. In addition pollen were counted because of their stratigraphic significance.

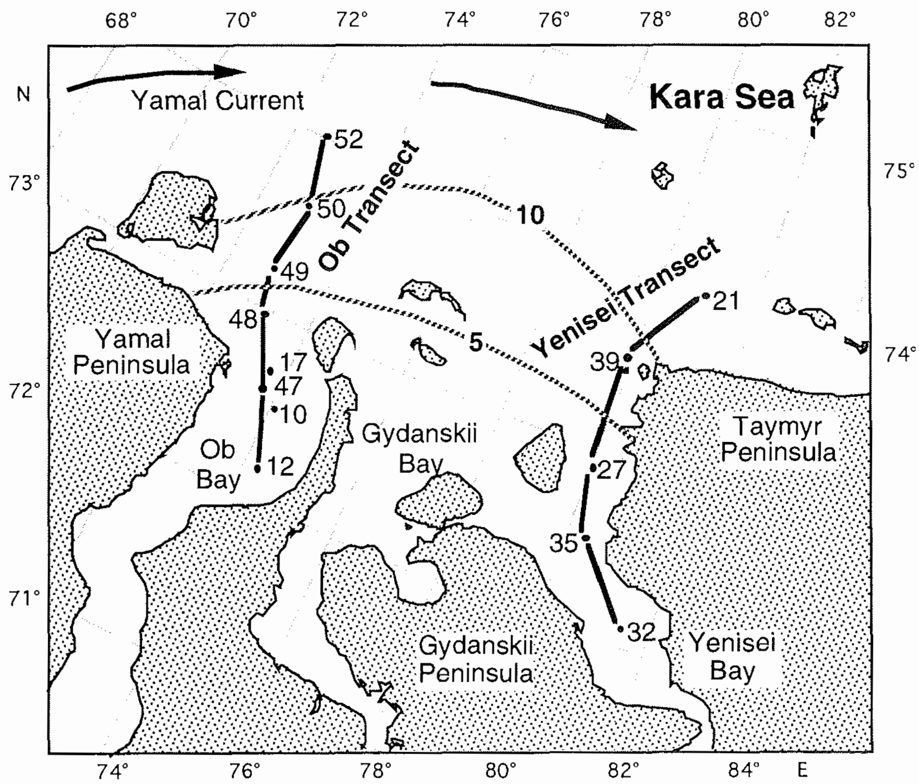

Fig. 1. Location of surface sediment samples along the Ob and Yenisei transects. The long-term mean surface salinity is taken from Burenkov and Vasil'kov (1995)

Material and Methods

During the expedition to the Kara Sea, surface sediments (multi corer cores 0-1cm) were sampled at 20 stations along four transects, of which 13 from the Ob and Yenisei transects are used in the present study (Fig. 1). The geographic coordinates are listed in Matthiessen, Stepanets et al. (this volume).

Freeze-dried samples were prepared with standard palynological preparation methods (e.g. Matthiessen, 1991, 1995). The processing method (application of cold HCl and HF) is similar to the method used to concentrate kerogen for maceral analysis in case of low TOC values. However, for palynological investigations the bulk of the detrital organic matter is removed by wet sieving in order to enrich the particulate organic matter larger than 6µm which can be more easily identified under the light microscope.

Concentrations were calculated according to the marker grain method of Stockmarr (1971). A known number of acetylosed *Lycopodium clavatum* spores were added to weighted dry sediment. Spore tabletts of the batch no.

124961 (distributed by Laboratory of Quaternary Biology at the Department of Quaternary Geology in Lund) were used with an average number of spores of 12,542 ± 2081. The spore were counted together with the palynomorphs.

The palynomorph concentrations p are calculated as

$$P\ (1/g) = \frac{n_p * n_s * 12{,}542}{n_L * w}$$

where

n_P: number of palynomorphs counted
n_S: number of tabletts added
n_L: number of *Lycopodium* spores counted
w: weight of dry sediment (g)

It has been estimated that changes in concentrations are significant in routine analysis when exceeding about half an order of magnitude (Matthiessen, 1995).

The taxonomy follows Matthiessen (1995), Rochon et al. (subm.) and Matthiessen and Brenner (1996). Palynomorphs were only counted when more than half of a specimen was seen. Only multi-chambered specimens of inner organic linings of benthic foraminifera were counted. Autofluorescence of palynomorphs was measured at an wave length of 450-490nm (ZEISS filter No. 9).

Table 1. Concentrations of selected palynomorph groups.

	Dinoflagellates (1/g)	Dinoflagellate Cysts (1/g)	*Pediastrum* (1/g)	*Botryococcus* (1/g)	Desmidiaceae (1/g)	Tintinnida (1/g)	Ciliate Cysts (1/g)	Benthic Foraminifer Linings (1/g)	Terrestrial Spores (1/g)	Bisaccate Pollen (1/g)	Other Pollen (1/g)	Total Pollen (1/g)	Bisaccate Pollen/Total Pollen	Pediastrum/Dinocysts
Ob Transect														
BP97-12	0	295	3182	147	236	29	295	29	354	2799	1178	4331	0.65	10.8
BP97-10	0	341	3380	236	419	0	393	131	393	3786	4428	8606	0.44	9.9
BP97-47	0	78	2671	156	182	0	337	156	104	2308	1530	3942	0.59	34.3
BP97-17	58	404	1635	212	135	173	462	231	289	1876	1578	3742	0.50	4.0
BP97-48	244	427	977	122	92	198	366	153	168	1519	1084	2770	0.55	2.3
BP97-49	626	766	961	70	14	557	599	223	237	2889	1183	4309	0.67	1.3
BP97-50	623	1916	1317	192	48	958	1245	479	239	2203	1509	3952	0.56	0.7
BP97-52	3022	2659	1015	97	0	991	1185	774	242	1656	363	2260	0.73	0.4
Yenisei Transect														
BP97-32	0	259	2244	86	1122	1122	1467	86	1036	41475	11480	53991	0.77	8.7
BP97-35	232	116	1852	58	1042	868	984	58	347	30188	49551	80086	0.38	16.0
BP97-27	96	96	1544	58	772	39	405	154	849	12089	5576	18514	0.65	16.0
BP97-39	213	766	502	50	113	226	1029	201	151	2768	954	3872	0.71	0.7
BP97-21	116	728	555	35	81	185	728	508	116	1739	578	2432	0.71	0.8

Results

All samples are dominated by terrestrial particulate organic matter (leaf cuticules, pollen etc.). This is reflected by the concentration of pollen that are higher in most samples than concentrations of all other aquatic palynomorphs. The distribution of phytoplankton (dinoflagellates, dinoflagellate cysts, chlorococcalean algae (*Pediastrum* spp., *Botryococcus* cf. *braunii* and desmidiacean algae), zooplankton (tintinnid loricae and ciliate cysts), zoobenthos (benthic foraminifer linings) and pollen are separately figured for the transects along Ob and Yenisei bays (Table 1; Figs. 2, 3).

Concentrations of thecate dinoflagellates principally increase along the Ob Transect offshore, while they remain fairly constant along the Yenisei Transect. Samples from the inner bays of both rivers are barren, while concentrations are larger than 3000/g at the northwestern station (St. 52) of the Ob Transect. Because species were not distinguished it is not possible to attribute these dinoflagellates to marine, brackish or freshwater environments. The increase offshore along the transects however suggests that they are most likely marine dinoflagellates.

The distribution of dinoflagellate cysts is comparable to that of the dinoflagellates. Cyst concentrations range from slightly less than 100 in the inner bays to more than 2500/g at the northwestern end of the Ob Transect. The assemblages in samples with statistically reasonable counts (> 50 specimens: Sts. 21,39,49,50,52) are dominated by the polar species *Algidasphaeridium*? *minutum* and related morphotypes (usually more than 70%), *Brigantedinium* spp. (up to 30%) and ?*Polykrikos* spp. sensu Kunz-Pirrung 1998 (5 to 10%). Species preferring relatively warmer waters (up to 10%) are dominated by *Operculodinium centrocarpum* sensu Wall & Dale with sparse occurrences of cysts of *Pentapharsodinium dalei* and *Spiniferites elongatus*.

The freshwater planktic algae (chlorococcalean algae *Pediastrum* spp. and *Botryococcus* cf. *braunii*, Desmidiaceae) show an inverse relationship to dinoflagellates and their cysts. *Pediastrum* spp. and desmidiacean algae decrease in concentrations to the inner Kara Sea by an order of magnitude while *B. cf.* braunii is more evenly distributed. *Pediastrum boryanum* and *P. kawraiskyi* are the dominant species. The freshwater signal of Ob and Yenisei may be distinguished because of the exclusive presence of *P. simplex* and *P. angulosum* in surface sediments and surface waters of the Ob Bay (see also Matthiessen and Boucsein, this volume). Additionally, individual desmidiacean species may show a different distribution but they were not distinguished at species level.

Fossilizable zooplankton species are represented by tintinnid loricae and ciliate cysts. The distribution of tintinnids does not show an unequivocal trend. Although most specimens can be assigned to *Tintinnopsis* spp. which may tolerate low sea-surface salinities (cf. also Matthiessen and Boucsein, this volume) highest occurrences occur both in the inner bays (Yenisei Transect) and inner Kara Sea (Ob Transect). Unfortunately, species assignment is even more difficult than for specimens from plankton samples because acids dissolve the minerals attached to the outer surface of *Tintinnopsis* specimens leaving only the inner organic wall. Occassionally, cladoceran carapaxes are present.

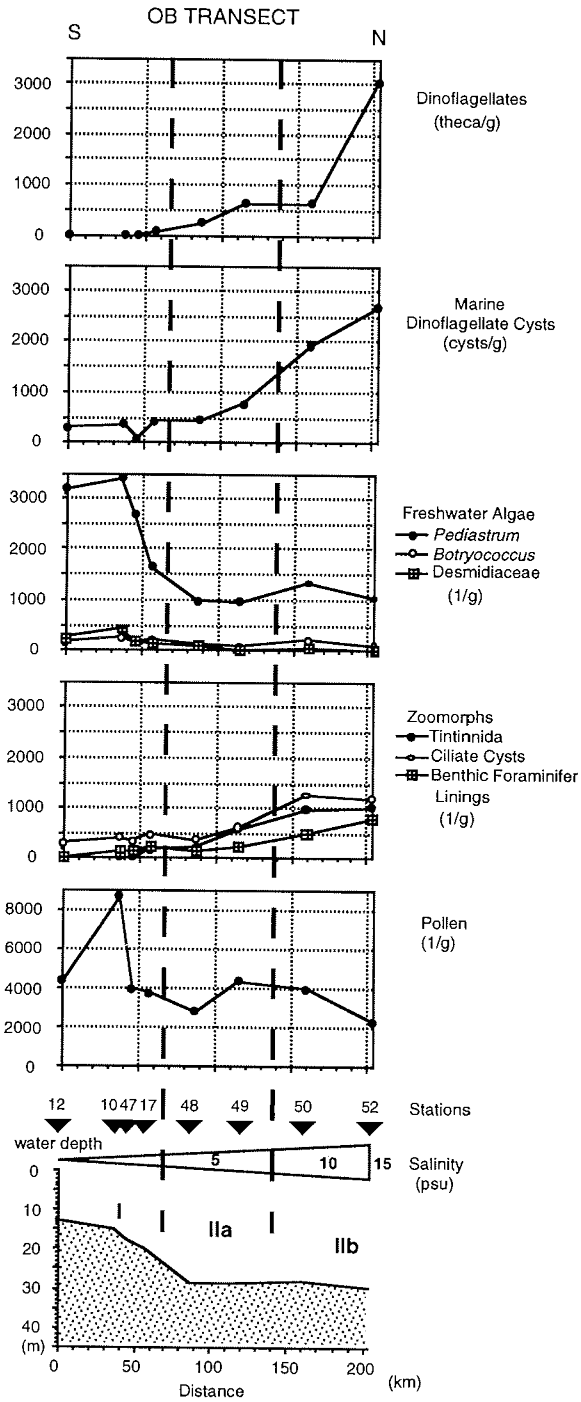

Fig. 2. Distribution of palynomorphs along the Ob Transect. Sea-surface salinities are from Burenkov and Vasilkov (1995). Facies zones I and II refer to figure 4.

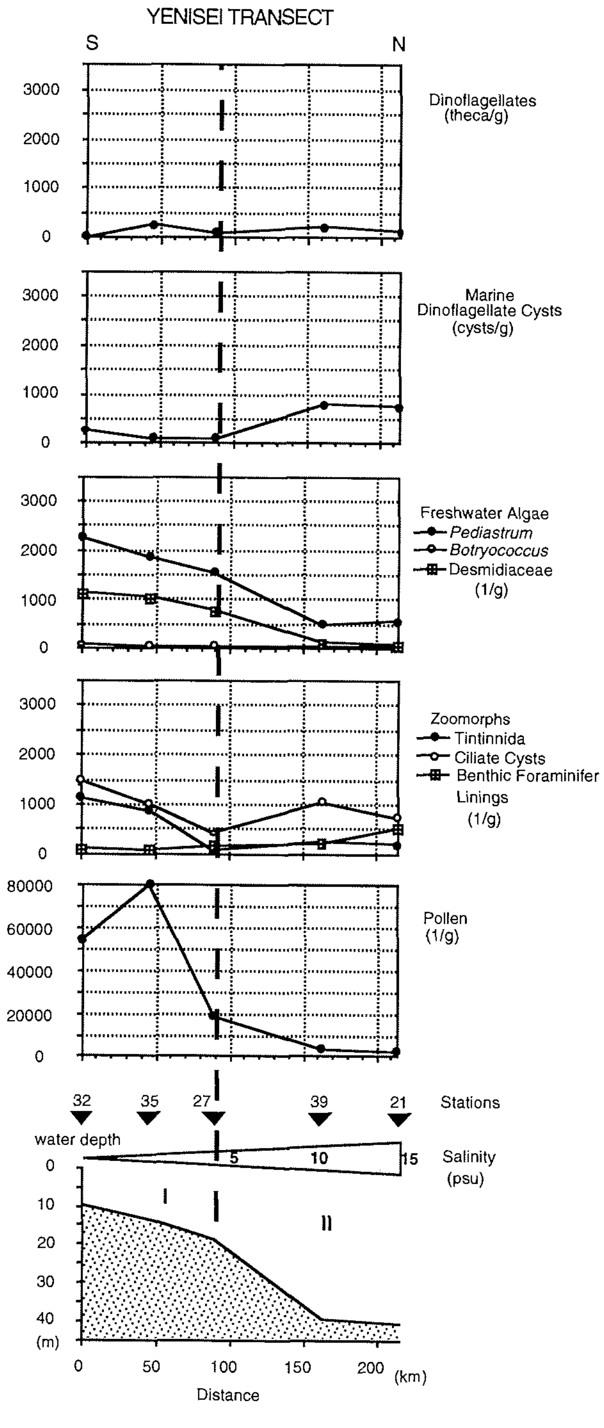

Fig. 3. Distribution of palynomorphs along the Yenisei Transect. Sea-surface salinities are from Burenkov and Vasilkov (1995). Facies zones I and II refer to figure 4.

Ciliate cysts show a variable distribution in surface sediments from the Yenisei Bay, whereas concentrations are slightly increasing along the Ob transect. This heterogenous distribution is probably due to the different ecological preferences of individual taxa which are summed up because of the absence of any taxonomy for ciliate cysts.

The benthic foraminifer linings are persistently present in all samples and generally increase in concentrations along the transects offshore.

The concentration of pollen is relatively uniform along the Ob Transect, whereas it decreases by an order of magnitude offshore along the Yenisei Transect. Bisaccate pollen are the dominant pollen group. The species composition differ significantly from surface water samples where bisaccate pollen are almost absent (Matthiessen and Boucsein, this volume). This is due to the fact that pollen in surface waters reflect only a seasonal signal, while pollen in sediments are naturally integrating the whole vegetation period of several years.

Discussion

Distribution of palynomorphs in relation to the salinity gradient
Previous investigations in estuarine environments of high northern latitudes showed that river discharge determines the composition of palynomorph assemblages (Mudie, 1992; de Vernal and Giroux, 1991; Kunz-Pirrung, 1998, in press). Assemblages in sediments underlying the freshwater plume off the Mackenzie River delta show a gradient in composition comparable to the transects in Ob and Yenisei. *Pediastrum* spp. and *Cosmarium* spp. (Desmidiaceae) are strongly decreasing in percentage abundances offshore whereas dinoflagellate cysts (*A.? minutum* s.l., *Brigantedinium* spp.) are strongly increasing (Mudie, 1992). Chlorococcalean algae dominate assemblages in the freshwater plume off the Lena River delta and off other rivers in the Laptev Sea, while dinoflagellate cysts are rare (Kunz-Pirrung, 1998, in press). Benthic foraminiferal linings are more uniformly distributed in the inner Laptev Sea than in the Ob and Yenisei bays. In the Estuary and Gulf of St. Lawrence dinoflagellate cysts and benthic foraminfer linings principally increase in concentrations with increasing salinities (de Vernal and Giroux, 1991).

Although a number of other aquatic palynomorph taxa (including acritarchs) were recorded from these low salinity environments, the chlorococcalean algae *Pediastrum* spp. and *B.* cf. *braunii* and desmidiacean algae are most useful indicators of freshwater discharge because they live exclusively in freshwater to slightly brackish waters and are usually well-preserved in the geological record. The occurrence of *Pediastrum* spp. in surface waters in the outer Ob and Yenisei estuaries correlates with high suspension concentrations (Matthiessen and Boucsein, this volume) showing the relationship between freshwater algae and riverine sediment influx. Relatively high concentrations of these algae in the sediments at the northernmost stations of both transects suggest that freshwater may be discharged seasonally further offshore than the data from the plankton survey in September 1997 suggests. In particular during the flood period in May to July riverine sediments with freshwater algae may be transported into the central Kara Sea.

The ecological preferences of fossilizable zooplankton is too little known in order to evaluate their significance as freshwater indicators. Tintinnids, ciliate cysts and benthic foraminifer linings might have a potential but it is at the moment difficult to assign their organic-walled tests to individual species due to the complex taxonomy and/or the unknown relation to certain species. Although all zoomorph groups can be quite abundant in arctic shelf seas (e.g. Laptev Sea, Kunz-Pirrung, 1998; in press), the distribution of individual morphotypes in relation to environmental gradients was not studied.

Few morphotypes of foraminifer linings can be assigned to certain benthic species (de Vernal et al., 1992). *Elphidium excavatum* is the only calcareous foraminifer in the sediment fraction > 125µm in Ob Bay with an organic lining (Korsun, this volume). Concentrations of benthic foraminifer linings correlate with the number of benthic foraminifer per $10cm^3$ sediment (r= 0.95) suggesting that concentrations of linings might be a rough proxy of benthic production. Accurate salinity preferences can not be determined for individual foraminifer recorded in the Ob Transect (for discussion see Korsun, this volume).

The dinoflagellate cysts recorded in this study are marine species which may tolerate low sea-surface salinities (e.g. Rochon et al., subm.; de Vernal et al., 1997). The outer bays are characterized by salinities in the range of 10 to 15psu according to compilations of historical data (Burenkov and Vasilkov, 1995). Their occurrence in the inner Laptev Sea (Kunz-Pirrung, 1998) at comparable salinities as in the Kara Sea suggests that *Algidasphaeridium*? *minutum* and related morphotypes, *Brigantedinium* spp. and ?*Polykrikos* spp. may tolerate salinities as low as 15psu but additional studies are required to assess salinity preferences.

The assemblages differ from those in the Laptev Sea in having higher abundances of species preferring relatively warmer waters. These species dominate assemblages from the innermost Barents Sea close to the Kara Strait (Rochon et al., subm.) and they may be transported eastward with the Yamal Current to the estuaries of Ob and Yenisei (Fig. 1).

The increase of concentrations by one order of magnitude along the transects reflects distinct changes in environmental conditions related to the average salinity increase along the transects. The low amounts in the inner Ob and Yenisei bays may be attributed to transport because compilation of historical data of sea-surface salinities showed that they are on average as low as 5psu (Burenkov and Vasilkov, 1995) which is much lower than the known salinity tolerance of species. However, the estuaries are characterized by strong interannual changes in sea-surface conditions. Thus dinoflagellate cysts might be produced in the few years of relatively high sea-surface salinities due to a lower discharge of freshwater in summer.

Distribution of pollen

Previous investigations showed that pollen concentration in marine sediments decreases across shelves exponentially with distance offshore (e.g. Muller, 1959; Mudie, 1982; Mudie and McCarthy, 1994; Rochon and de Vernal, 1994). Mudie (1982) compiled data showing that pollen load of large rivers is mainly deposited near the river mouths. This trend is also obvious in the inner Kara Sea where inner shelf sediments are already depleted in pollen by a factor of

2 (Ob) to 20 (Yenisei) compared to the outer estuaries (Figs. 2, 3). A comparable trend is observed in the Laptev Sea, where pollen decrease strongly offshore (Naidina and Bauch, 1998).

The relative importance of fluvial vs. atmospheric transport in the investigation area is not known. A peak of pollen concentrations on both transects at sea-surface salinities of less than 5psu show that significant amounts of pollen are deposited when freshwater comes into contact with saline water. Therefore, riverine waters are probably the major transport agent for pollen from source areas in the hinterland of the Kara Sea to the shelf whereas atmospheric transport is probably negligible.

Pollen records may be skewed by differential transport of pollen and terrestrial spores (e.g. Mudie, 1982; Mudie and McCarthy, 1994; Rochon and de Vernal, 1994). During transport bisaccate pollen may be preferentially enriched because of their floating capability. Therefore, the pollen spectra in the surface sediments do not reflect the local terrestrial vegetation because of the overrepresentation of bisaccate pollen. This is probably a characteristic feature of Siberian estuarine environments. Naidina and Bauch (in press) observed a similar trend in the eastern Laptev Sea off the Lena Delta. The relatively constant ratio of bisaccate pollen to total pollen along the transects (Table 1) indicates that differential sedimentation of pollen is not of major importance in the inner coastal zone. Therefore, pollen analysis may have some potential to resolve stratigraphic problems in the coastal regions of the Kara Sea, and may allow to correlate terrestrial with marine paleoenvironmental records.

Characterization of the environment with palynomorphs
Concentrations of palynomorphs change distinctly along both transects around 73° 30´N between stations 49 and 50, and 27 and 39, respectively (Figs. 2 and 3) allowing to define zones (Fig. 4).

Facies Zone I is characterized by a predominance of freshwater algae and high concentrations of pollen which sharply decline at the transition to the inner Kara Sea. Relatively high TOC values (Boucsein et al., this volume), clay fraction contents (Müller and Stein, this volume) and suspension load in the water column (Lukashin et al., this volume) correlate with the maximum concentrations and indicate a riverine source of organic carbon and fine-grained sediments. The major part of riverine sediments may be deposited at salinites below 5psu.

Facies Zone II is characterized by low concentrations of freshwater algae and pollen, and an increase in concentrations of marine dinoflagellate cysts and benthic foraminifer linings. Two subzones IIa and IIb may be distinguished in Ob Bay because of an significant increase of dinoflagellate cysts at stations 50 and 52 indicating a stronger influence of marine waters in the northwestern part of the investigation area. The sample coverage in both estuaries however is too small to recognize possible strong local variability in composition of assemblages in the estuaries.

Polyakova (this volume) observed a comparable trend in diatom distribution. Freshwater diatoms dominate assemblages south of latitude 73° 30´N. She suggested that this change indicates the location of the average frontal zone where strong horizontal gradients in salinity occur. Today, freshwater phytoplankton transported by the rivers into the Kara Sea and/or produced locally in the low salinity surface waters may dominate the phytoplankton south of latitude 73°N whereas autochthonous marine production may be more important in the Kara Sea. Thus both aquatic palynomorphs and diatoms may be useful indicators of sources of aquatic particulate organic matter.

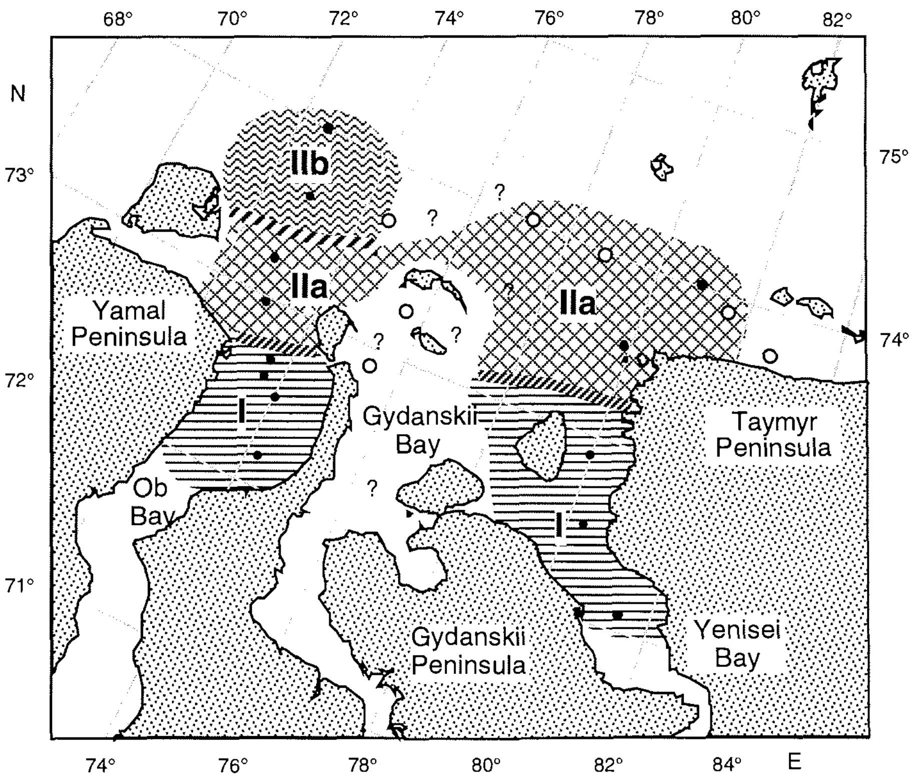

Fig. 4. Distribution palynomorph assemblages in the investigation area (open circles: samples to be analysed).
Facies Zone I: Dominance of freshwater palynomorphs in surface sediments;
Facies Zone II: Increase in marine palynomorphs in surface sediments.

Characterization of aquatic organic matter
The palynological analysis revealed that aquatic organic matter in the bays of Ob and Yenisei is composed of planktic and benthic production from different environments because of the mixing of freshwater with marine water. The marine organic matter in surface sediments can not be easily attributed to primary production because in addition to phytoplankton both zooplankton (tinntinids, ciliate cysts) and zoobenthos (benthic foraminifers) contribute to palynomorph assemblages.

The increase in marine aquatic palynomorphs principally agrees with the increase of marine macerals along the transects offshore (Boucsein et al., this volume). However, aquatic production may be underestimated by maceral microscopy which distinguishes particles based on their epifluorescence character. Certain groups of aquatic palynomorphs can not be seen because of the absence of autofluorescence. Thus, all polar dinoflagellate cysts (*A.? minutum, Brigantedinium* spp., ?*Polykrikos* spp.) as well as benthic foraminifer linings do not have autofluorescence. Fluorescence character of dinoflagellate cysts varies between major groups probably related to chemical composition of the cyst wall and the nutritional strategy of their vegetative stages (cf. Matthiessen, 1995). Cysts of phototrophic species (*O. centrocarpum, P. dalei, S. elongatus*) principally show autofluorescence whereas cysts of heterotrophic (probably all polar taxa in the Kara Sea) species do not. However, it must be mentioned that fluorescence character is not a stable feature because age of palynomorphs and facies of sediments influence the fluorescence. Thus, reworked palynomorphs such as dinoflagellate cysts may have no fluorescence (cf. Matthiessen, 1996).

Palynological investigations on the other hand are hampered by the optical resolution of light microscopes. Microfossils having a size of less than 5µm or even much larger may not be related to a specific biological group due to its small size and/or preservation, and palynomorph fragments are not counted. Therefore, palynomorphs may give insight into the biological composition of particulate organic matter but quantitative estimation of individual proportions of e.g. marine and freshwater origin are not feasible. Palynological investigations are thus an additional tracer approach such as geochemical investigations on biomarker. The bulk composition of particulate organic matter may be better described with maceral microscopy (Boucsein et al., this volume).

Preservation of palynomorphs

Both terrestrial and aquatic palynomorphs may be affected by biogeochemical degradation although they are composed of relatively stable chemical compounds. Aquatic palynomorphs such as dinoflagellates are usually easily degraded during settling through the water column because of their fragile theca composed of cellulose-like material. Therefore they are rarely recorded in sediment traps from deep waters (Dale and Dale, 1992) and in surface sediments from shelves (Kunz-Pirrung, 1998). However, under specific sedimentary conditions dinoflagellates may be preserved in Holocene shelf sediments such as the laminated sediments from Saanich Inlet (western Canada) which were deposited under anoxic conditions (Mudie, 1998).

The presence in surface sediments may indicate that recently after a bloom massive sedimentation of dinoflagellates occurred. After sampling the surface sediments were immediately frozen preventing further organic matter degradation. This signal has a low preservation potential under natural conditions.

Selective preservation of pollen may also distort pollen spectra (e.g. Havinga, 1984; Nadina and Bauch, 1998).

Ob and Yenisei bays - possible source areas of sea-ice sediments?

The southern Kara Sea may be an important source area for sea-ice sediments (Pfirmann et al., 1997). They tracked sediments sampled on ice floes in the Siberian Branch of the Transpolar Drift north of Svalbard back to the inner shelf off the rivers Ob and Yenisei. These sea-ice sediments contained high abundances of the clay mineral smectite (>63%) and planktic freshwater diatoms (>70%) which are characteristic for the surface sediments from facies zone I (Müller and Stein, this volume; Wahsner et al., subm.; Polyakova, this volume). This association of clay minerals and diatoms is unique for the Eurasian shelf seas. Surface sediments from the easternmost Laptev Sea contain high abundances of freshwater diatoms while smectite contents are low, whereas in the western Laptev Sea marine diatoms and smectite dominate (Cremer, 1998; Wahsner et al., in press).

Palynomorphs may be an additional indicator for facies of sea-ice sediment source areas. A palynomorph assemblage in a sea-ice sediment sample collected northeast of Svalbard (83°21´N, 32°51´E) in the Siberian Branch of the Transpolar Drift has a comparable composition as sediments in facies zone I in the inner bays of Ob and Yenisei. Terrestrial and freshwater palynomorphs clearly dominate the assemblages. Pollen are more abundant than aquatic palynomorphs and the ratio of *Pediastrum* to dinoflagellate cysts (7.5) is high (Table 1).

The freshwater palynomorphs co-occur with high smectite contents in surface waters and sediments (Müller and Stein, this volume), and freshwater diatoms (Polyakova, this volume). The riverine sediments may be directly discharged onto the sea ice during break up in spring, or resuspended from the river bottom at shallow depths (<20m) into sea ice during freeze-up in autumn. Then these sediments may be transported with sea ice via the Transpolar Drift as far north as the Fram Strait (cf. Pfirman et al., 1997).

Dispersal with sea ice might be a common phenomena not only for clastic sediments but also for microfossils such as palynomorphs and diatoms. Occurrence of displaced freshwater microfossils in deep-sea sediments may be easily explained with sea-ice transport. A multiparameter approach (e.g. Pfirman et al., 1997) may help to better define both location (clay minerals, heavy minerals) and facies of source areas (coastal zones or open shelf sea with diatoms and palynomorphs) of sea-ice sediments.

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