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Geochemistry of the Ob and Yenisey Estuaries: A Comparative Study

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**Viacheslav V. Gordeev, Bettina Beeskow,
Volker Rachold**

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1 Introduction

The rivers of the Russian Arctic along with the adjacent areas of the coastal seas represent the largest regional system within which the interaction between land and ocean takes place.

Two of the biggest Arctic rivers, the Ob and Yenisey share similar features. Their catchment's areas have the same origin, occupy large parts of West Siberia, are located in similar climate zones, their main streams are directed from south to north and both rivers have small deltas and big and long estuaries. Annually, the Ob and Yenisey deliver 404 and 620 km^3 of water to the Kara Sea, respectively (Mikhailov, 1997; Gordeev, 2000, 2004). The estuaries with N-S extension of hundreds of kilometers are distinctive due to significant geological differences within the catchment area.

During the last 20 years Arctic rivers have been increasingly attracting attention for several reasons:

1. The Polar Regions are the most sensitive to global climatic changes (Walsh, 1991) and the predicted temperature increase due to global warming has a strong impact to the coastal areas (Houghton et al., 1996).
2. The reliable assessment of present conditions of the coastal and marine ecosystems in the Arctic region is important to avoid possible ecological problems caused by planned exploitation of new oil and gas deposits in the region.
3. Of great scientific interest is the study of transport and transformation processes within the estuarine area and the influence of climatic changes on the behaviour of dissolved and particulate suspended matter including pollutants in the transition zone between river and sea (marginal filters - Lisitzin, 1994).

For several decades, the input of water and suspended sediment of Ob and Yenisey have been monitored by the Hydrometeorological Survey of the former Soviet Union and Roskomhydromet in Russia. The observation of suspended sediment fluxes began between 1938 and 1942. Subsequently, geochemical examination of dissolved and suspended matter was initiated. The first investigations of major and trace elements in dissolved and particulate material in the Russian Arctic rivers were started in the early 1950s within the framework of the USSR Hydrometeorological Survey (Konovalov, 1959; Konovalov et al., 1968). Similar studies were carried out by specialists of the Geological Institute of the USSR Academy of Sciences (Glagoleva, 1959; Nesterova, 1960; Kontorovitch, 1968; Lubchenko and Belova, 1973) under leadership of Acad. N.M. Strakhov (Strakhov, 1961-1963). However, for trace metals in particulate and dissolved material no adequate methods of sampling, treatment and analysis were developed at this time. Metallic samplers, paper filters and the low sensitivity of analytical chemical-spectral methods did not allow the collection of reliable data, especially for dissolved trace elements.

The monitoring of heavy metal (HM) concentrations in river water of the Russian Arctic was carried out in the last two decades of the 20th last century by the State System of

Observations and Control for Environment Pollution of the State Committee on Hydrometeorology of the USSR. Based on these results and with financial support of the AMAP (Arctic Monitoring Assessment Program), the "Atlas of environment pollution of aquatoria of the Russian Arctic coastal seas", 1999 (S.A. Melnikov - editor) was prepared. The multi-annual average concentrations of Fe, Mn, Cu, Zn, Ni, Co, Cd, Pb, Cr and Sn in unfiltered water samples of seven Arctic rivers, including Ob and Yenisey, were presented. Unfortunately, the interpretation of these data is questionable because unfiltered water samples were analysed.

Contemporary geochemical investigations of suspended sediment and bottom sediment of the Russian Arctic rivers were carried out for the first time in 1969 (Morozov et al., 1974).

Modern methods of sampling and analyses of heavy metals in water and suspended matter of Ob, Yenisey and Lena Rivers were applied during three expeditions to the Laptev and Kara Sea within the framework of the Russian-French-Netherlands Program SPASIBA (Scientific Program on Arctic and Siberian Aquatoria) between 1989 and 1993. The results have been published in a series of papers (Martin et al., 1993; Gordeev and Sidorov, 1993; Kravtsov et al., 1994; Dai and Martin, 1995; Gordeev and Shevchenko, 1995; Guieu et al., 1996; Cossa et al., 1996; Cauwet and Sidorov, 1996; Nolting et al., 1996 and other) and show that the earlier concentrations of dissolved HMs had been significantly overestimated. In fact, the typical HM concentration in dissolved and particulate material of the lower courses of the Arctic rivers is similar or even lower than the average concentration of the global river discharge.

Since 1994, complex geochemical investigations have been carried out in frameworks of two Russian-German programs: "The Laptev Sea System" and "Siberian Rivers Run-off" (SIRRO). The results were published in two fundamental books: "Land-Ocean Systems in the Siberian Arctic. Dynamics and History", Kassens et al.- eds., 1999, and "Siberian river run-off in the Kara Sea. Characterization, quantification, variability and environmental significance", Stein et al. - eds., 2003, and in a series of papers on Ob, Yenisey, Lena, Yana, Khatanga River geochemistry (Rachold et al., 1996; Rachold, 1999; Rachold and Hubberten, 1999; Lara et al., 1998; Lukashin et al., 1999; Schoster et al., 2000; Kohler et al., 2003; Gordeev et al., 2004 and other). At the same time, significant contributions to geochemical problems of the Russian Arctic rivers were made by specialists from the USA (e.g. Moran and Woods, 1997; Guay and Folkner, 1998; Huh et al., 1998).

In 1996, Shvartsev et al. declared that within the last few decades a dramatic decrease of river water quality has led to significant changes in the ecosystem of the Ob River basin. One year later, the International Research Center on Physics of Environment and Ecology, the Siberian branch of the Russian Academy of Sciences, established a complex ecological research program for the Ob basin. Three expeditions and two workshops "Ecology of the Poymas of Siberian rivers and Arctic" (1999, 2000) were organized and scientific reports including the results of HM determinations in the middle part of the Ob River and some of its tributaries were published (Shvartsev et al.,1996, 1999; Sorokovikova et al., 1999; Leonova et al., 2000; Kovalskaya et al., 2002; Sazonova and Shvartsev, 2002; Gordeev et al., 2004; Gordeev and Vlasova, 2002).

In recent years (June 2001, December 2001, and September 2002) expeditions to the lower course of the Ob and Yenisey Rivers took place under the auspices of the P.P.Shirshov Institute of Oceanology RAS. The upper Ob Estuary and Yenisey Estuary have been investigated during the 38-th and 39-th cruises of the R/V "Academic Boris Petrov" to the Kara Sea in 2002 and 2003 (Schoster F. and Levitan M.A., 2003, 2004). The results of these cruises are not yet published.

The objective of this work is to provide a comprehensive geochemical characteristic of the two largest Siberian rivers - Ob and Yenisey. In this course, all available published and unpublished geochemical data of Ob and Yenisey Rivers and Estuaries are summarized and new assessments of average concentrations of dissolved and particulate heavy metals, organic carbon, nutrients and their gross and net fluxes to the Arctic Ocean presented. The main processes of biogeochemical transformation of the riverine sedimentary material in water column of the estuarine-deltaic zones of the Ob and Yenisey are discussed, as these processes influence the geochemical characteristic of bottom sediments in the estuaries and adjacent areas of the Kara Sea.

2 The characteristics of catchment and estuarine-deltaic areas

2.1 Watershed geology

The Ob and Yenisey basins occupy the huge territory of the West Siberia (Fig.1). The West Siberian Plane is the vast weak-elevated (up to 150-170 m above sea level) plane, with low inclination to the north, high moistening and weak drainage by surface waters that caused high level of bogging up. The greatest in the World marsh system Vasuyganie between the middle Ob and Irtysh Rivers occupies the territory of approximately 800x350 km with the level of bogging up to 70% (Panina, 1972). The West Siberian Plane is covered with the Quaternary marine and continental sedimentary deposits up to 50-100 m thickness. The Neogene rocks under sediment cover are revealed to the surface along the river valleys only. The north extremity of the Sayan-Altai mountain country edges the Ob basin in south (Kuznets Alatau – up to 2200 m asl, granites, basalts, diabases are distributed; Salaire ridge – Palaeozoic crystalline limestones, sandstones, shales, tufa, granites; Kuznets hollow – coal stratums up to 10 m.).

The Yenisey basin occupies the east extremity of the West Siberian Plane as the narrow belt (100-250 km) from the north spurs of the East Sayan to the Kara Sea, consisted of Cretaceous continental deposits. The eastern part of the Yenisey basin occupies the Mid Siberian platform. The late Proterozoic Sayan-Yenisey folded zone is subdivided into the four parts. (1) The East-Sayan in the south consists of folded gneisses and schists, intruded by granite massifs. (2) Northward follows the Angara-Kansk fold system, which is mainly built up of Archaic aluminum and feldspar gneisses and (3) the Angara-Tungus fold system composed of folded carbonates, terrigenous series, mafite and gneisses. (4) Sand- and mudstones, as well as carbonate layers characterize the northernmost Turukhansk fold system. The northern edge of the Mid Siberian platform, presented by the Putorana mountains (1400-1700 m asl), comes abruptly to the North Siberian (Taimir) lowland limited by the Byrranga mountains in the north. Shales, limestone, sandstones and other sedimentary rocks are distributed in the Putorana Plato, as well as the magmatic rocks – basalts, diabases and other rocks of similar composition.

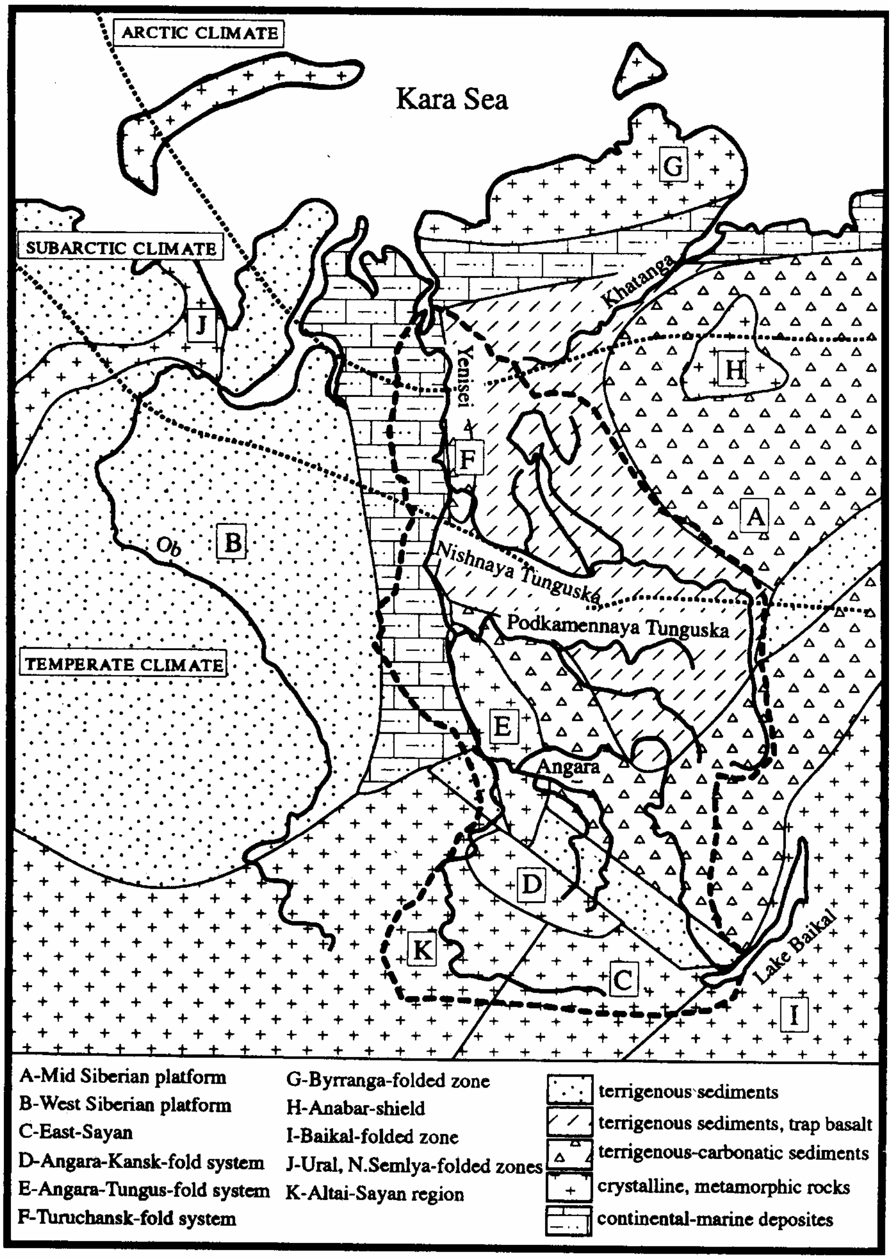


Figure 1 **Geological overview of the Ob and Yenisey drainage basins (Nalivkin, 1967; Panina, 1972; Dolginov and Kropatshyow, 1994; Beeskow and Rachold, 2003).**

2.2 Estuarine-deltaic areas

The postglacial transgression of the World Ocean has resulted in flooding of the eroded river valleys which have been formed in the conditions of regression of the sea. As a result, the stretched ingression bays Ob Guba and Yenisey Bay were formed and mainly filled by river waters. At the top of these bays the deltas are forming at present. Therefore the mouth areas of the Ob and Yenisey Rivers are related to the estuarine-deltaic type (Mikhailov, 1997).

The Ob Guba

The mouth area of the Ob River constitutes a unit together with the mouth areas of the Nadym, Pur and Taz Rivers.

The outlet near Salekhard, 287 km from the sea-delta transition, is considered to be the top of the Ob mouth area. The Ob delta comprises two parts: the northern zone - the system of the Khamanel Ob with multiple river arms and islands, and the southern zone - the wide and shallow Nadym Ob. The area of the Ob delta is 3250 km^2 of which 40% is attributed to islands (Ivanov, 1980) (Fig.2).

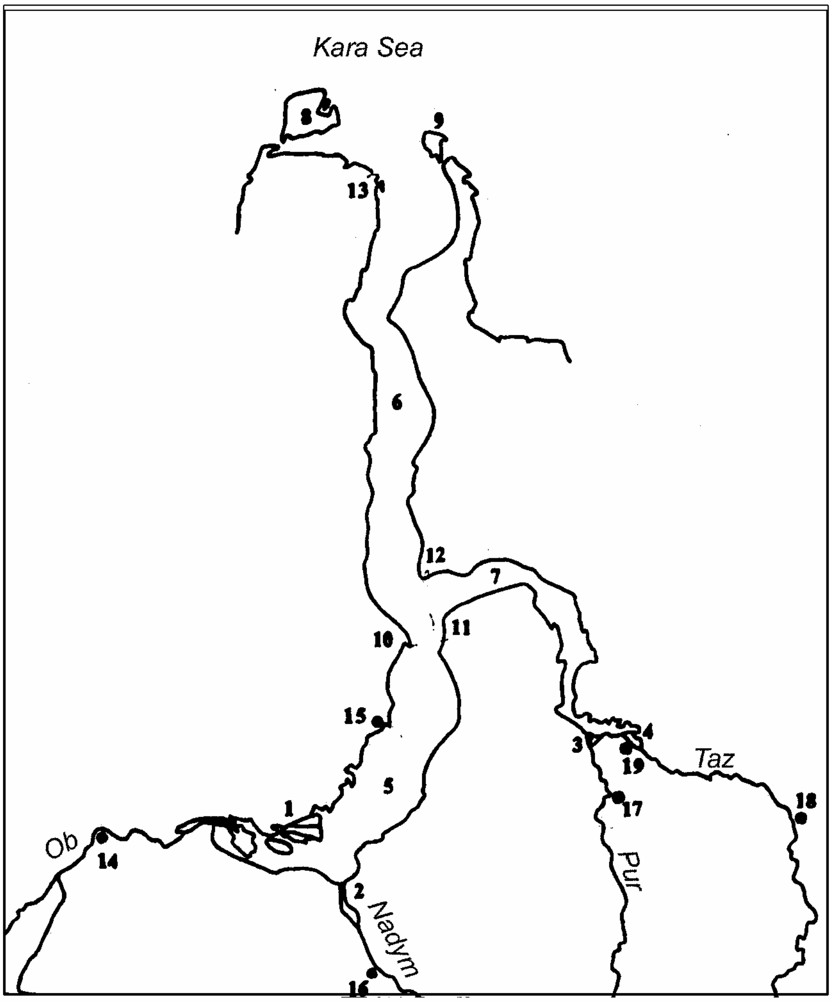


Figure 2 The mouth areas of the Ob, Nadym, Pur and Taz (Mikhailov, 1997). Deltas: 1 - Ob, 2 - Nadym, 3 - Pur, 4 - Taz; the parts of the Ob-Taz Guba: 5 - southern, 6 - northern, 7 - Taz guba; islands: 8 - Belyi, 9 - Shokalsky; Capes: 10 - Kamennyi, 11 - Kruglyi, 12 - Trehbugornyi, 13 - Poyelavo; Settlements: 14 - Salekhard, 15 - Novyi Port, 16 - Nadym, 17 - Samburg, 18 - Sidorovsk, 19 - Tazovsky.

The Ob Guba is 760 km in length from the Ob delta to the exit into the Kara Sea and covers an area of 40800 km^2. The Ob Guba width varies from 35 to 80 km, with depths between 10 and 12 m. The length and area of the Taz Guba are 300 km and 7750 km^2, a width is 7-48 km (Ivanov, 1980). The total area of the Ob-Taz Guba is 48550 km^2, respectively. The total area of mouth area is 55000 km^2.

At time of spring flood the water level is high with an average of 6.5 m near Salekhard and about 1 m near the sea edge of the delta. In low water periods (from mid of July to mid of October) the northern and NE winds form wind-induced surges up to 3 m at the sea edge of the Ob Guba. Semidiurnal tides between 0.3 and 0.4 m are observed in the Ob mouth. At low water the surges may spread up to 350 km from the sea edge, the tides - up to 50 km, i.e. they are stopped in the Guba area (Ivanov, 1970). The maximum river water current in periods of high water may exceed 1m/s. Saline waters cannot penetrate to the southern part of the Ob Guba during the whole year.

The water temperature in the Ob Guba increases in summer up to 16.5° C. First ice appearance is between 15 and 25 October, the average time of ice breaking is the 1 June (Ivanov et al., 1980).

The average total water discharge into Ob Guba is 497.7 km^3/y of which Ob, Nadym, Taz and Pur contribute 404, 18, 32.3 and 43.4 km^3, respectively. In combination with the local run-off of 34.8 km^3 from the Ob Guba and Taz Guba shores the freshwater import to the sea is estimated to be 532.5 km^3/y (Mikhailov, 1997). The volume of the Ob Guba is 400 km^3.

The fresh water volume annually withdrawn on ice cover formation in the Guba and returned after thawing comprises 65-70 km^3.

The average multi-annual salinity at surface (A) and bottom (B) in August in the Ob and Yenisey Estuaries are given in Fig. 3 (Harms et al., 2003).

The vertical distribution of water temperature and salinity at the sections along the Ob Guba is shown below in Fig. 4. In autumn 1993, during the 49th cruise of the R/V "Dmitry Mendeleev", measurements of both temperature and salinity were carried out from 68°50' N to 76° N along 73° E latitude (Figure 4 A and B). The wide frontal zone from approximately 73°30' N to 71° N may be detected in this section. The water temperature decreases from south to north from 7° C to 2.5° C, and the salinity increases from 1‰ to 16‰. In average, the temperature decreases by 0.017 °C and salinity increases by 0.055 ‰ per km. That is lower than typical values for the frontal zones in the World Ocean (Fedorov, 1983).

The temperature and salinity distributions along the transect from 72°10' N to 73°54'N (Fig. 4 C and D) have been recorded in September 1997 during the 28th cruise of R/V "Academic Boris Petrov". Churun and Ivanov (1998) show the clearly pronounced two-layer structure of the water masses with the warm upper freshwater layer and the cold saline bottom layer. A pronounced pycnocline with a thickness of 7-8 m divides these two layers. A narrow frontal zone of about 10 km width where the salinity increases from 3 to 10-12‰ has been observed. The horizontal gradients of surface temperature and salinity equal 0.07 °C/km and 0.3 ‰/km, respectively.

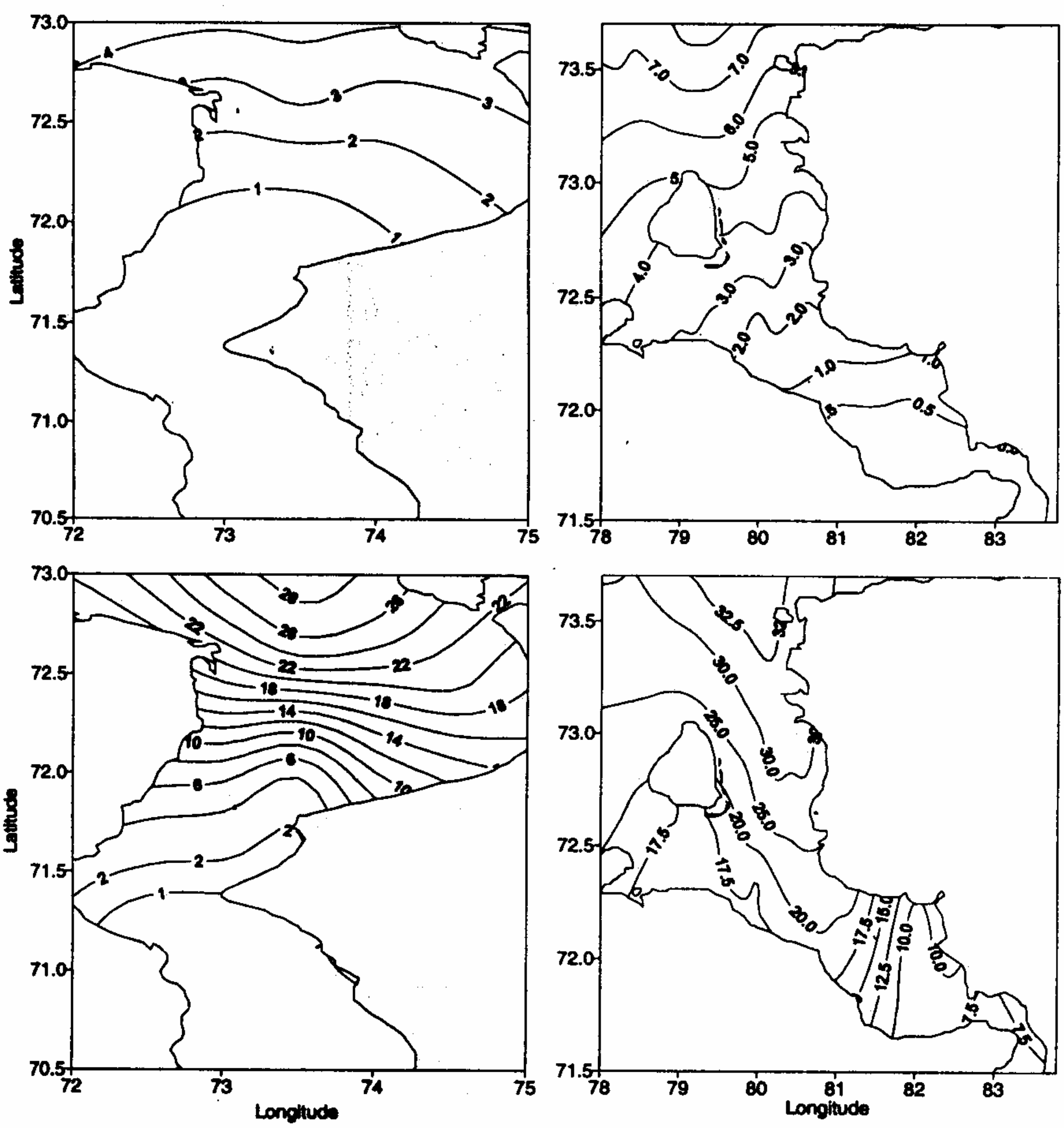


Figure 3 **Average multiannual salinity distribution at the surface (A) at the bottom (B) in August in the Ob Estuary (left) and the Yenisey Estuary (right) (Harms et al., 2003).**

10 days later, a further transect along the Ob Estuary was carried out (Fig. 4 E and F). Here, the frontal zone was not observed. Compared to the first record the surface temperature decreased by 4-5 °C and the surface salinity increased up to 13.8-20.8‰. Salinity and temperature distribution in August-September 1999 is shown in Fig.4 G and H.

This shows the fast changes in spatial T and S distribution in the Ob Guba. However, generally the two-layer structure is typical and the so-called salt-wedge type is characteristic for the Ob estuarine-deltaic system.

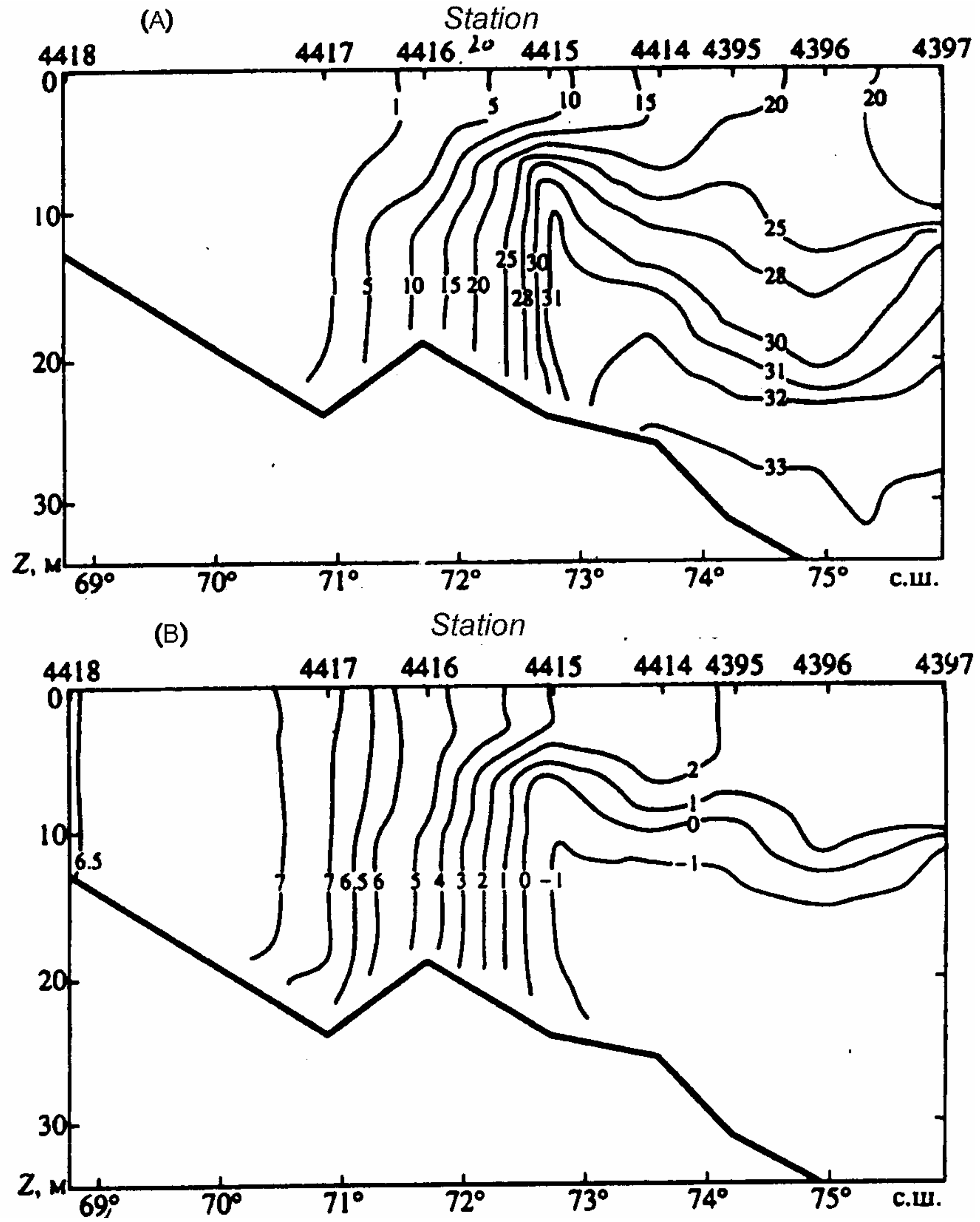
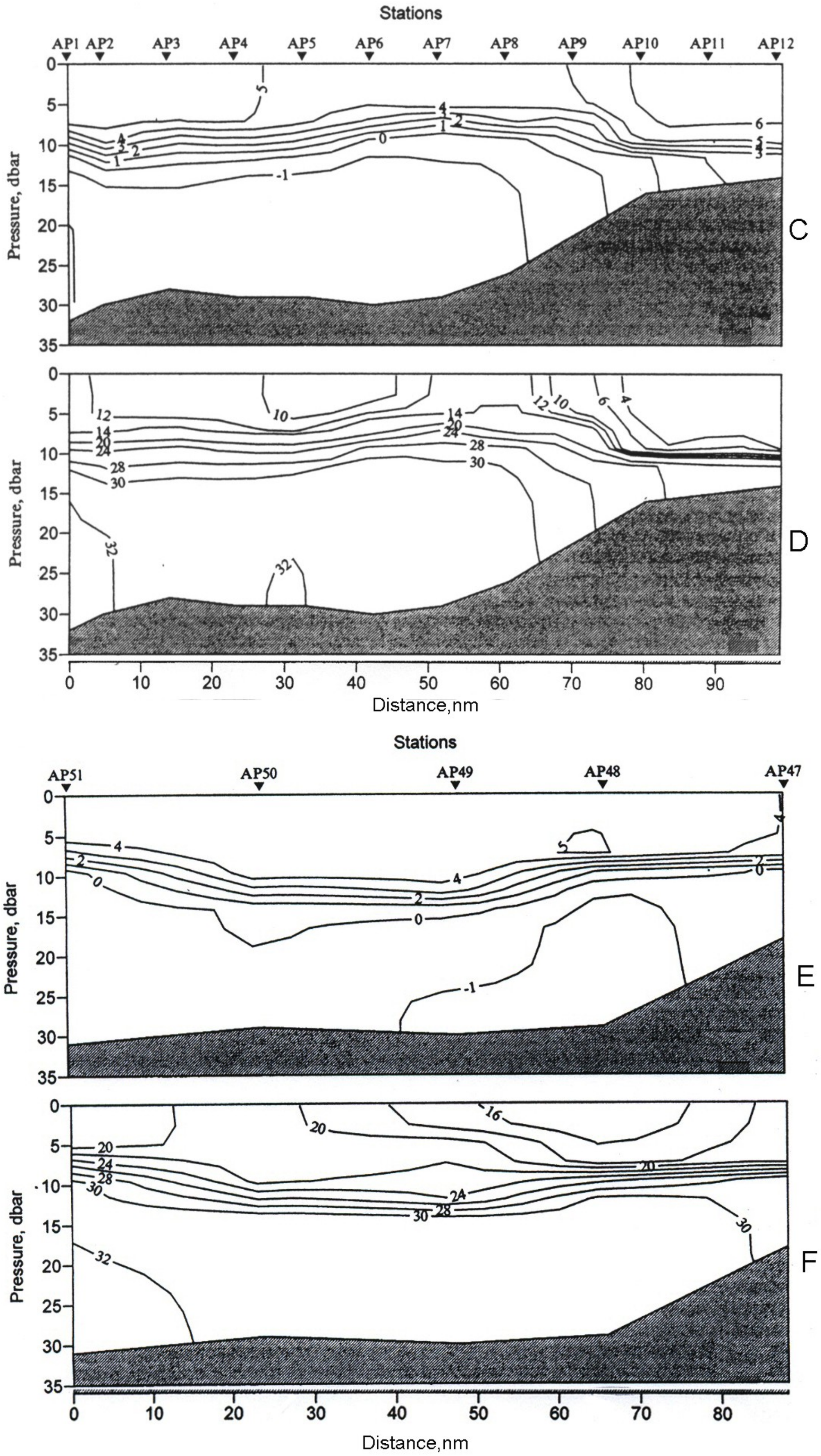


Figure 4 **(A-H). Distribution of salinity and temperature in the Ob estuary: A(salinity) and B (temperature) in September 19-27, 1993 (Burenkov and Vasilkov, 1994); C (temperature) and D (salinity) in September 13-15, 1997, E (temperature) and F (salinity) in September 22-23, 1997 (Churun and Ivanov, 1998), G (salinity) and H (temperature) in August 24-September 7, 1999 (Stephantsev and Shmelkov, 1999).**



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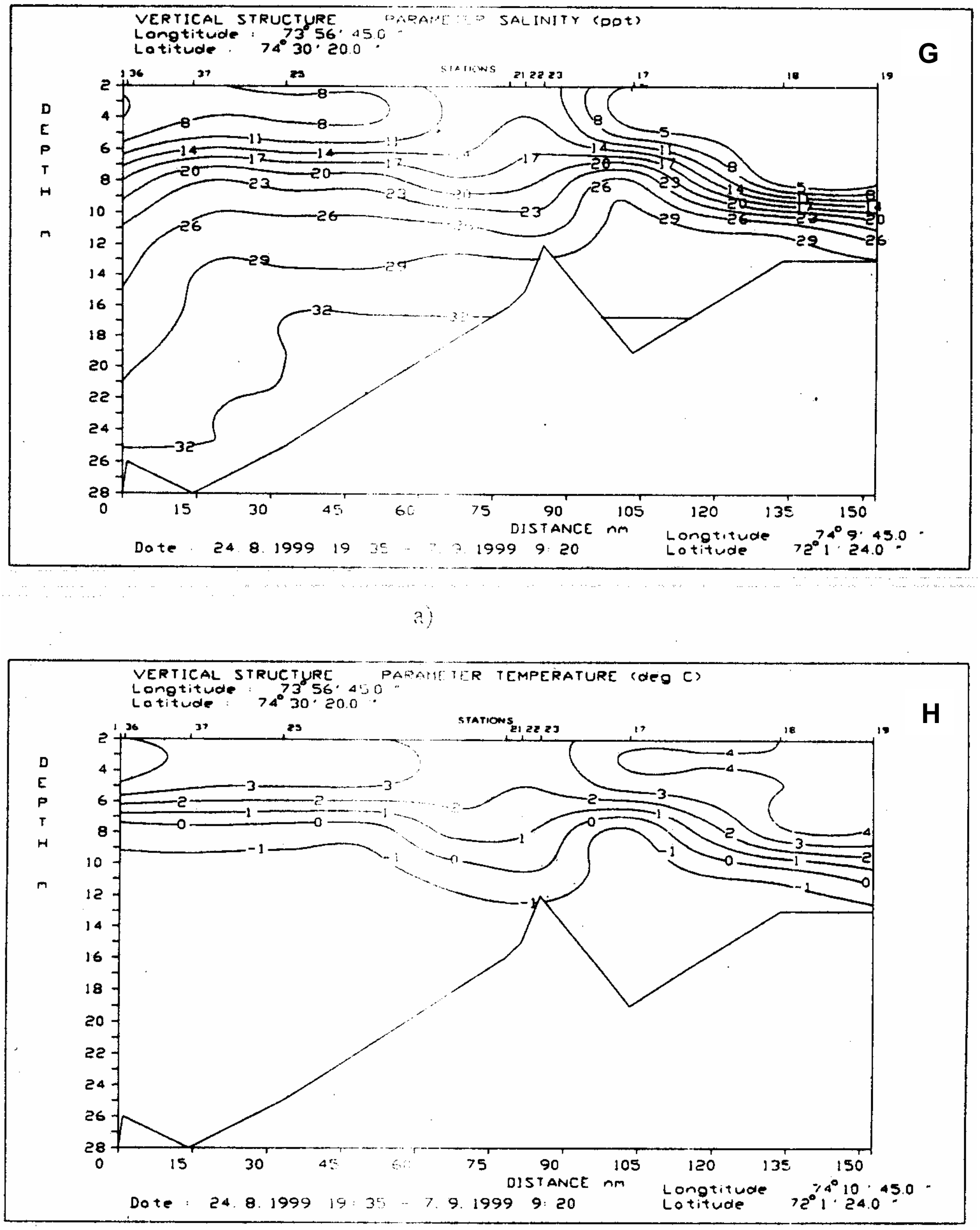


Figure 4 continued.

The Yenisey Bay

The top of the Yenisey delta is located near Ust Port (Fig. 5). The delta consists of a ramified system of arms the majority of which are very shallow. The delta is 196 km in length and covers an area of 4500 km^2 (Mikhailov et al., 1982).

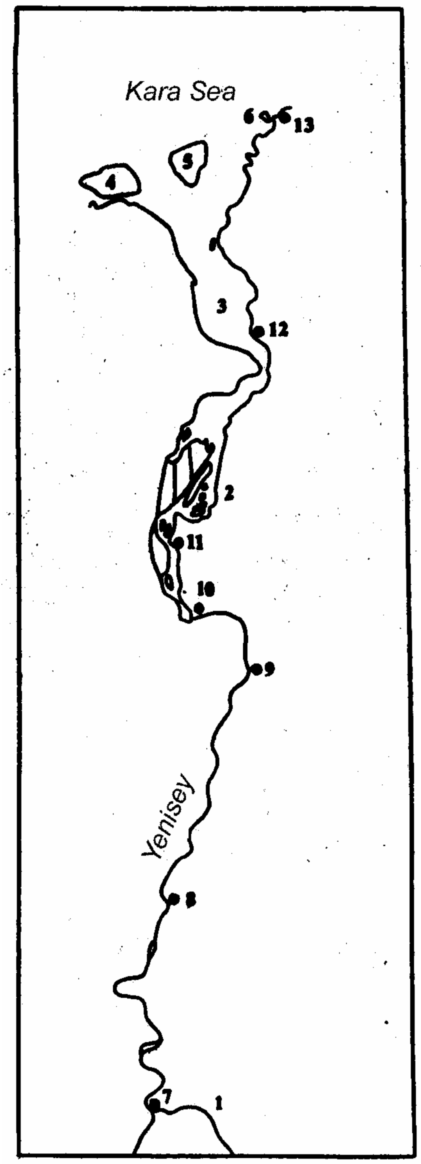


Figure 5 **The mouth area of the Yenisey River (Mikhailov, 1997).**
1 - Nizhnyaya Tunguska, 2 - delta of Yenisey, 3 - Yenisey Bay; islands: 4 - Oleniy, 5 - Sibiryakov, 6 - Dixon; settlements: 7 - Turukhansk, 8 - Igarka, 9 - Dudinka, 10 - Ust-Port, 11 - Karaul, 12 - Sopochnaya Karga, 13 - Dixon.

The Yenisey bay is divided in two parts: the southern one from the marine edge of the delta to the cape Sopochnaya Karga with a length 121 km, and the northern one - up to the exit to the Kara Sea near island Dixon with a length 230 km and total area 20000 km^2. The total length of the estuarine-deltaic system of the Yenisey (delta plus estuary) equals 547 km and total area 24500 km^2. The wind-induced variations of the water level at the sea edge of the delta are about 2-3 m. The surges may penetrate in periods of low waters up to the point of the confluence of the Yenisey with its tributary Nijnaya Tunguska (about 870 km from the sea edge of the delta) (Ivanov and Osipova, 1974). The tide variations near the sea edge of the delta may reach 0.3-0.5 m.

After the construction of the dams the penetration of the tides has been reduced to 445 km inwards from the sea edge of the delta. In contrast, before the mid 1960s the penetration at summer-autumn low water period was reached 743 km (to the Kureika River mouth) (Graevsky, 1987)

The water currents during high water are 0.8-1.2 m/sec, during low water it ranges between 0.3 and 0.5 m/sec. At time of high surges and tides the reverse currents may appear, particularly in the delta area and sea water penetrate into the delta.

Ice formation begins in average between 9th and 13th of October. The typical ice thickness during winter is 1.5-1.9 m. The ice break at the top of delta (near st. Karaul) starts normally on the 10th of June, and the ice run begins around the 19th of June.

Near Igarka, the ice break takes place between the end of May and beginning of June. The penetration of seawater into the Yenisey Bay is typical for the pre-spring period when the bay is covered by ice and the run-off is small. The waters with salinity 20-30‰ and temperature –0.05° - –1.5°C may reach the sea edge of the delta (Balkarov et al., 1989; Mikhailov, 1997).

In flood time the bay is totally filled with fresh water for up to 20 days. Distribution of temperature and salinity at the section along the Yenisey Bay in autumn 1993, during the 49-th cruise of the R/V "Dmitry Mendeleev", is shown in Fig. 6 A and B (Burenkov and Vasilkov, 1994). In general, the distribution is similar to that of the Ob Guba. Two frontal zones are visible: the first front between station 4401 and 4400 with a width about 2.5 km and the second front between station 4410 and 4413. In the first frontal zone the horizontal temperature gradient is about 1 °C/km and the difference in salinity is 8‰ (in the upper 10 m layer only). The second frontal zone takes up the whole water column.

The saline water (S>20‰) spreads along the sea bed up to 71°30'N due to north -south directed near-bottom current. On the return of the R/V "Dmitry Mendeleev" 3-4 days later, the first sharp thermal front near 74°N had practically disappeared.

In September 1997, during the 28-th cruise of the R/V “Acad. Boris Petrov” (Fig. 8), the measurements of T and S on transect in the Yenisey Estuary were carried out twice within a short interval of 1-2 days (Fig. 6 C, D and E, F). The usual two-layer stratification of the water column is visible and there are only small differences between the two profiles.

The salinity distribution of the Yenisey Estuary in summer 1995, 2000 and 2001 (Fig. 6 I, K and L) indicates a very sharp horizontal salinity gradient just above the sill into the river delta and a strong stratification further seaward. These figures show clearly the phenomenon of “salt intrusion”, the penetration of saline bottom waters into the estuary. Here, the saline bottom waters moved upstream of the sill into the river delta. This phenomenon occurs with different intensity in different years and seasons (Harms et al., 2003). Similar patterns of S and T distribution in the Yenisey Bay were observed in 1999 and 2003 (Fig. 6 G, H, M and N)

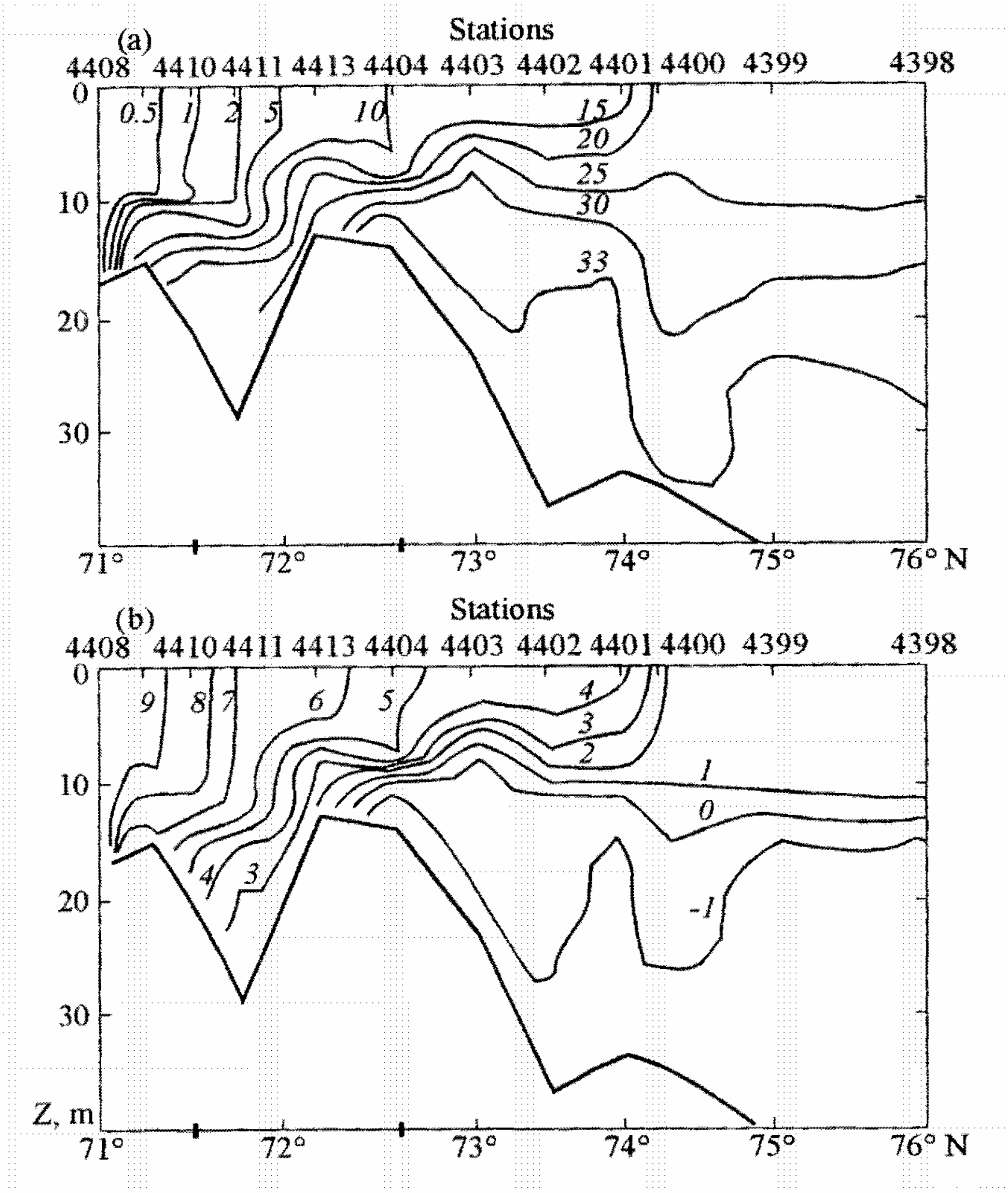
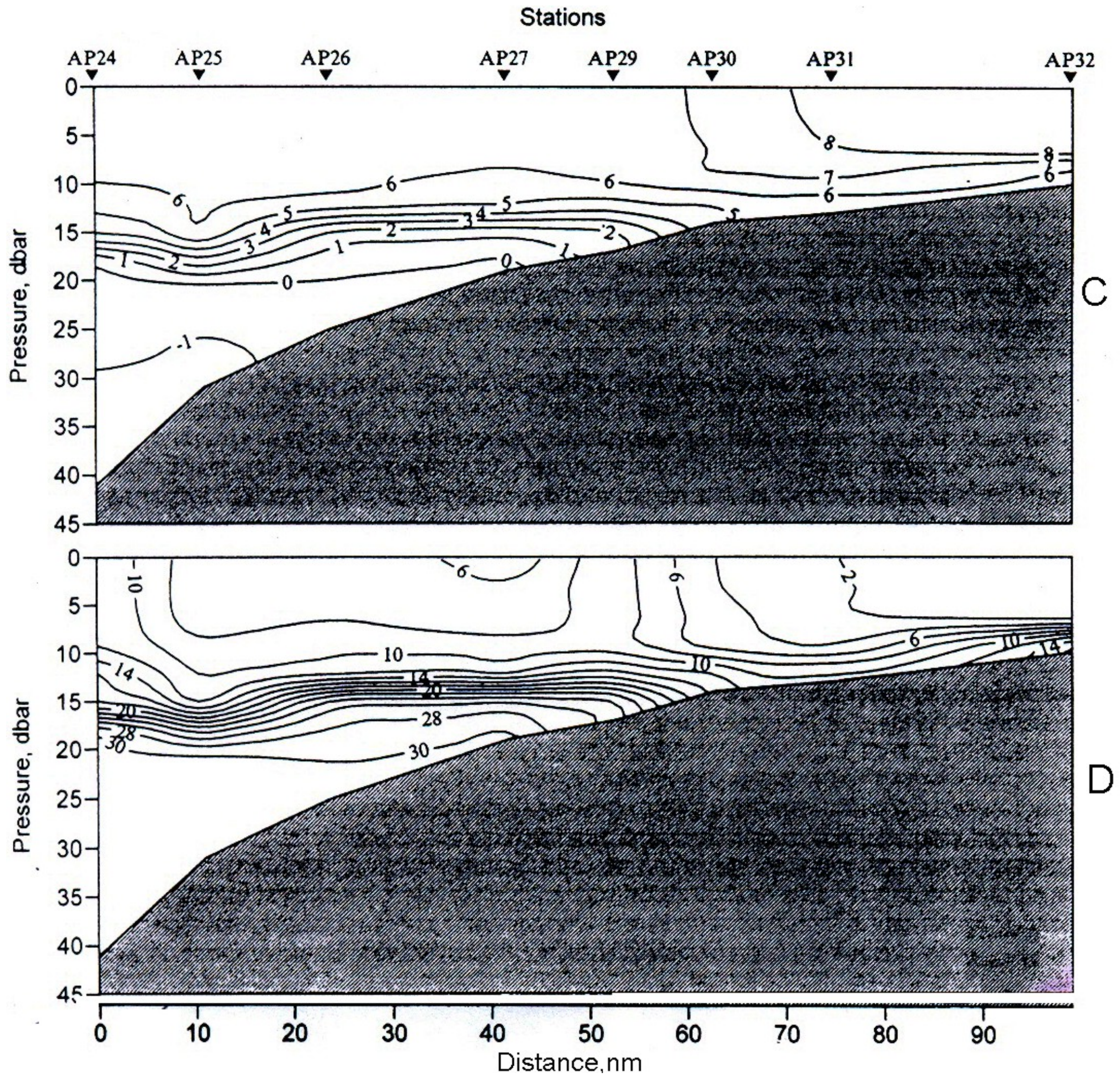


Figure 6 Distribution of salinity and temperature in the Yenisey Estuary: A (salinity) and B (temperature) in September 19-27, 1993 (Burenkov and Vasilkov, 1994), C (temperature) and D (salinity) in September 17-18, 1997, E (temperature) and F (salinity) in September 19-20, 1997 (Churun and Ivanov, 1998); G (salinity) and H (temperature) in August 26 - September 6, 1999 (Stephantsev and Shmelkov, 1999); I, K and L - salinity in summer 2001, summer 2000 and summer 1995 (Harmes et al., 2003); M (temperature) and N (salinity) in August 19-24, 2003 (Shmelkov et al., 2004).



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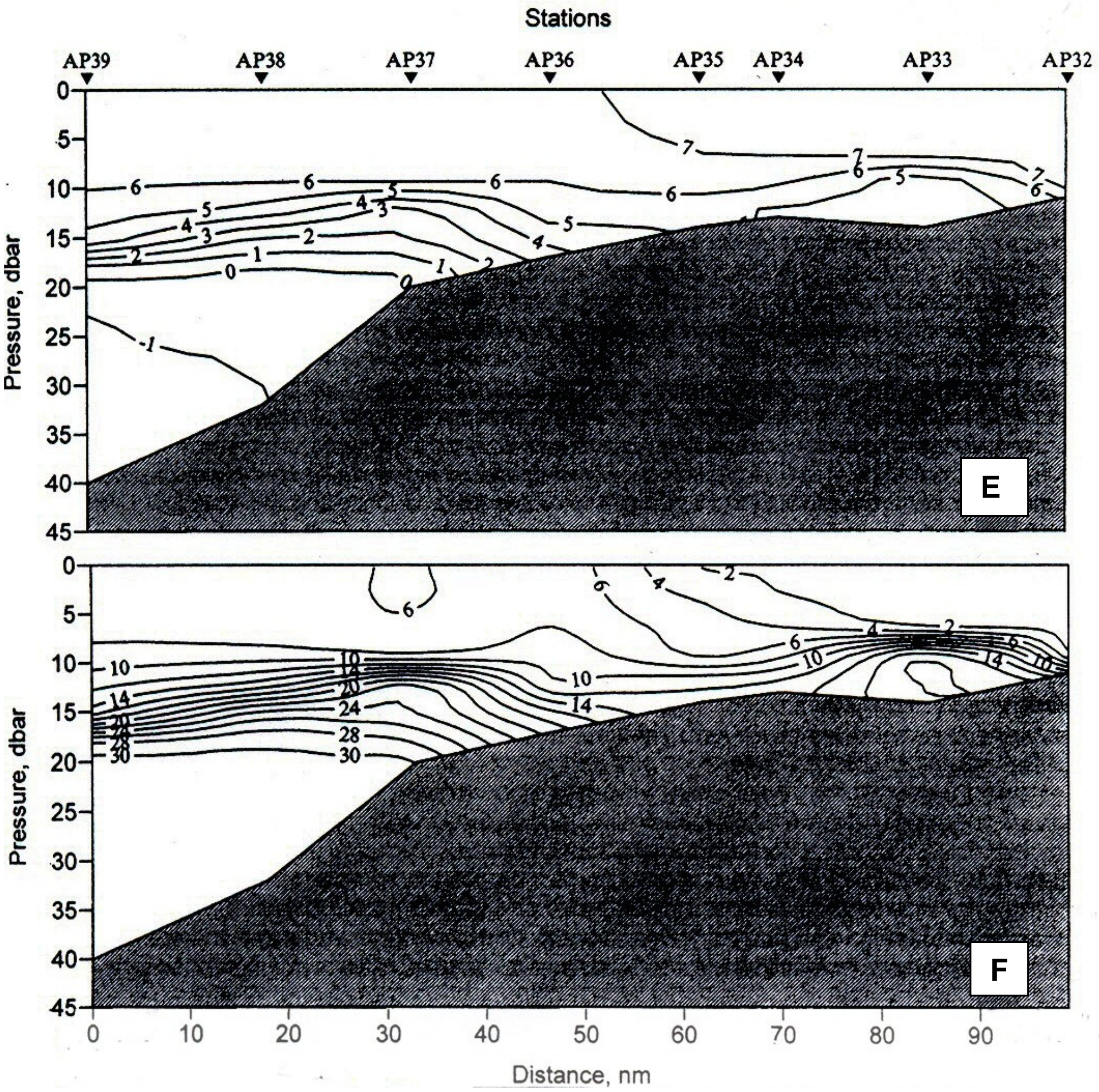

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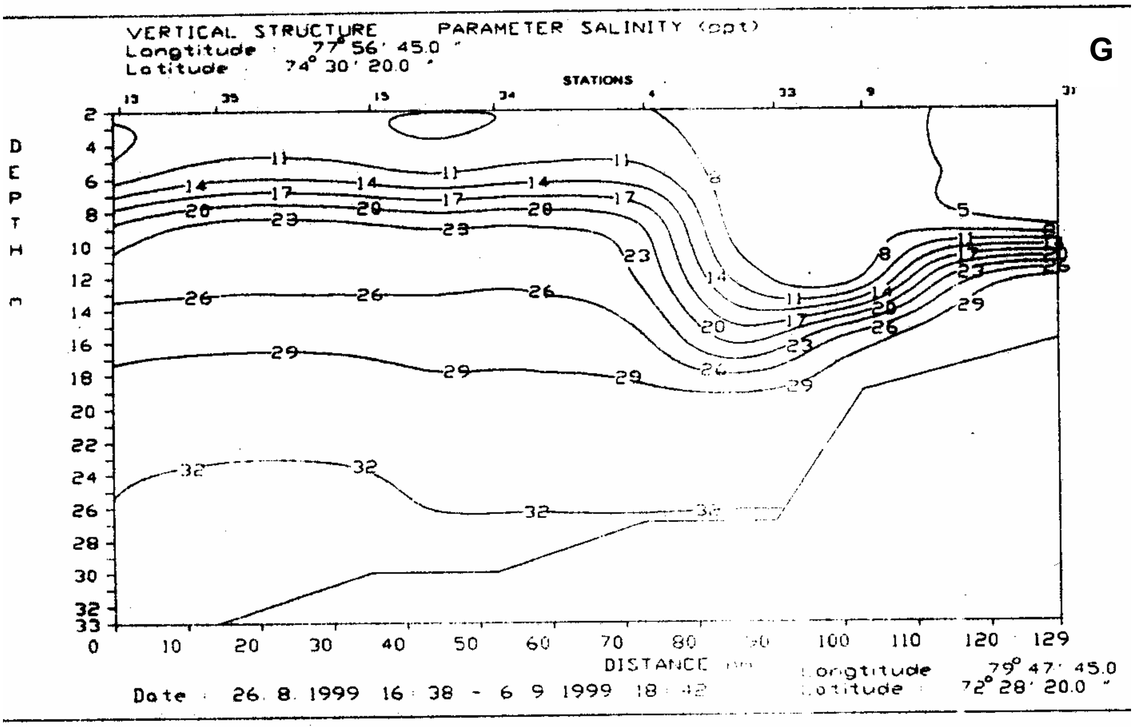

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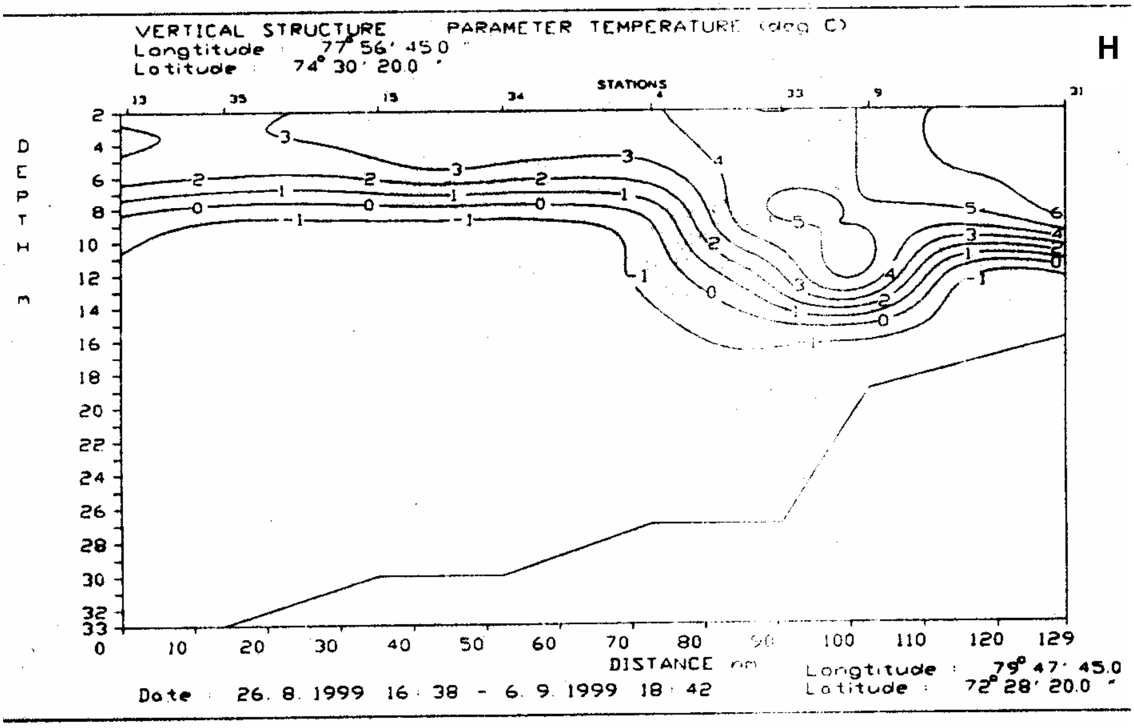

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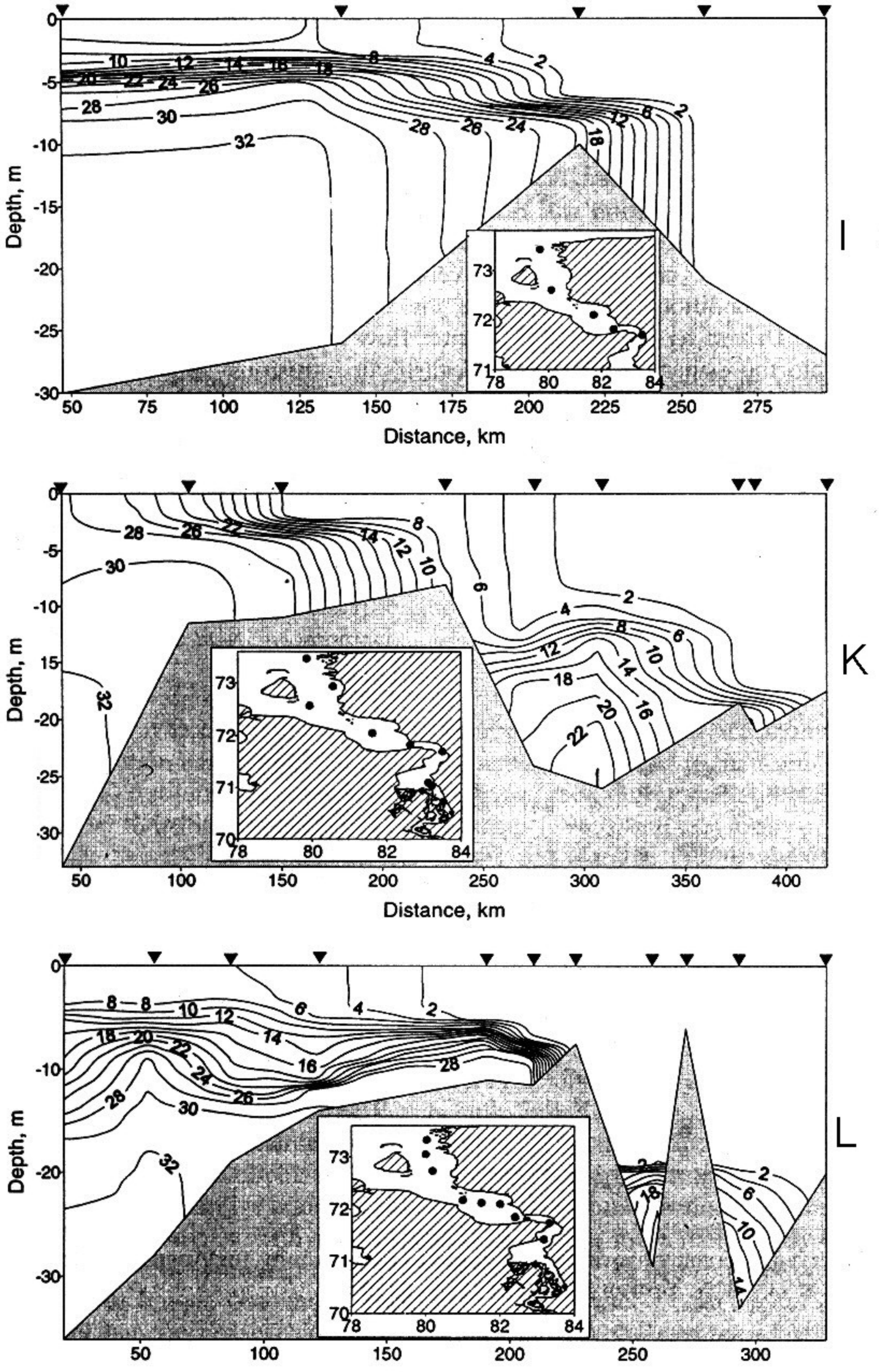

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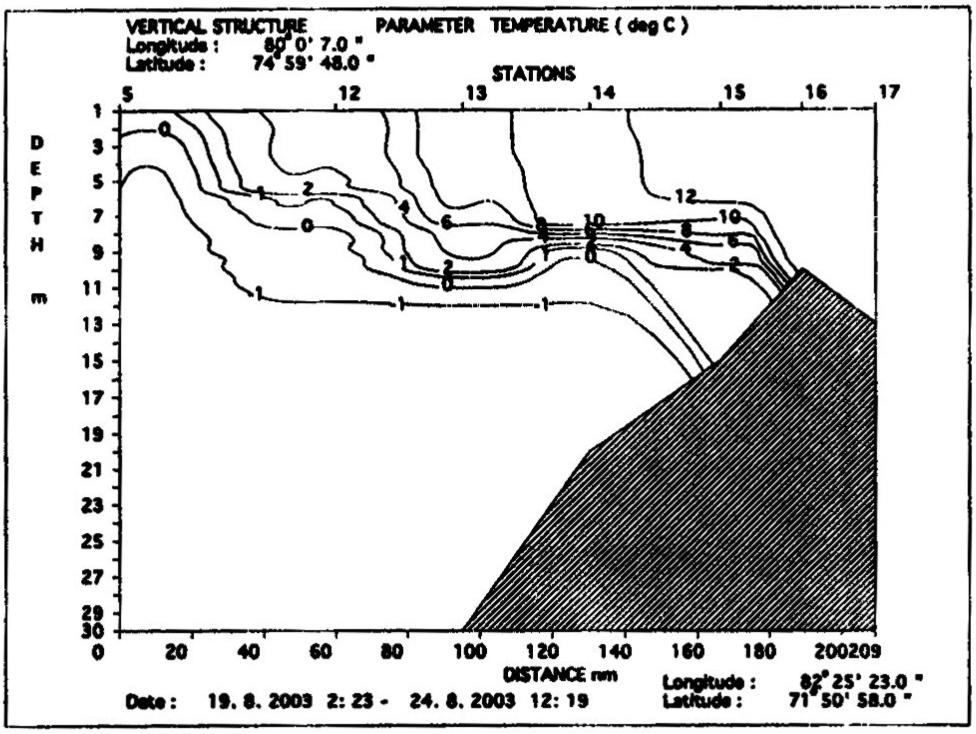

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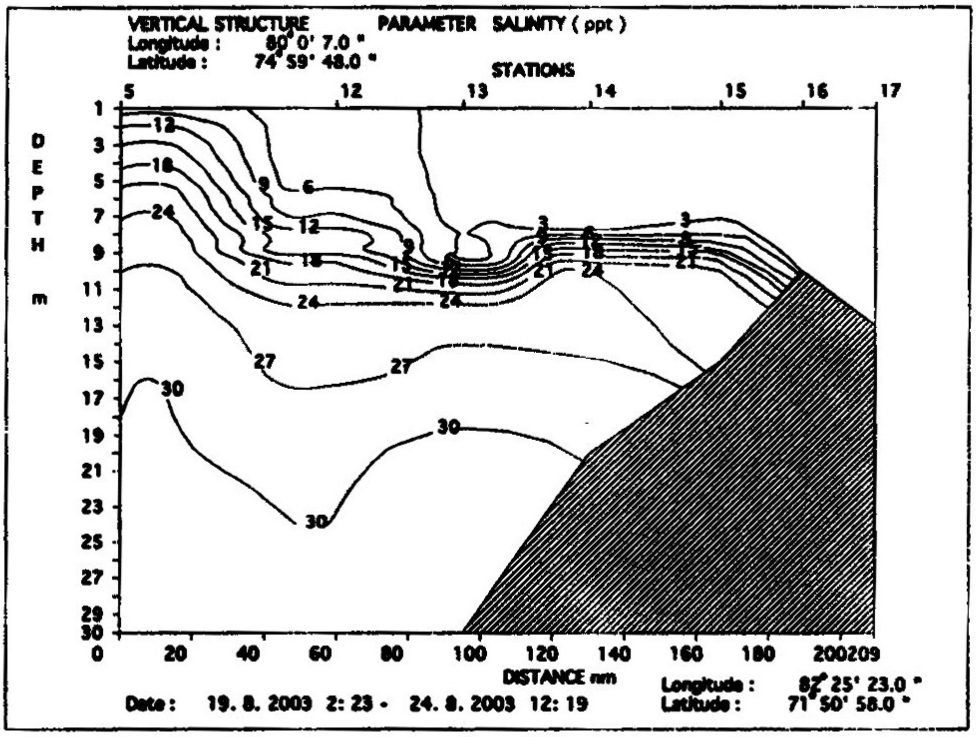

N

Figure 6 continued.

3 Materials and methods

In this section the description of sampling, sample treatment and analyses is given. This is done, for the expeditions where publications were done first.

3.1 49-th cruise of the R/V "Dmitry Mendeleev" (1993)

The 49-th cruise of the R/V “Dmitry Mendeleev” was carried out in the Kara Sea and in the estuaries of Ob and Yenisey from 15 August to 15 October 1993 in the framework of the international programs JGOFS and SPASIBA. The sampling locations are shown in Fig. 7. Water samples were collected by a Rosette system with 24 Niskin bottles (1.8 l) and by a large plastic bottle with a sampling volume of 150 l. The concentration of inorganic dissolved nutrients (NO_2, NO_3, NH_4, PO_4 and Si) was determined on board ship immediately after sampling. A Technicon Analyzer II with standard method was used according to Makkaveev and Stunjhas (1994).

The water samples were filtered through pre-weighted nucleopore filters (0.4 µm pore size, 47 mm diameter) to obtain suspended particulate matter (SPM) for geochemical analyses and electron probe X-ray analyses (EPXMA). SPM was also separated for particulate organic carbon (POC) determinations using Whatman glass fibre filters.

The industrial separator SAJ-3M with the rotation rate 6000 rot/min and productivity 1200 l/hour was used to separate the water samples. Water was soaked into the separator in the low part of the vessel at 5m depth in motion during 4-10 hours depends on suspended matter concentration. In this way, the average samples along a defined distance up to 30-50 miles and in a certain range of salinity (in a range of several per mille) were obtained.

Surface sediments were collected by a grab samples "Ocean-0.25", a gravitation tube of a large diameter and a box-corer (Fig.7).

The grain size separation of suspended material and bottom sediment were carried out by elutriation (Regnier and Wollast, 1993). To do so, the sample is suspended in water and submitted to vertical water current. The velocity of this current is adjusted to remove selectively material of a defined grain size fraction. The procedure is based on the Stokes law of sedimentation. The device permits the separation of samples into fractions in the range between 4 to 50 µm. The fine fractions were filtered through the pre-weighted membrane filters, dried, weighted and removed from the filters by ultrasonic treatment. This procedure was applied to four samples of bottom sediments (station 4397, 4399, 4409 and 4417) with separation of the fractions >50, >32, >16, >8, >4 and <4µm. Due to the small amount of the suspended matter towards the sea sample materials of different stations were combined (Yenisey: 2+7=Y1- 2 and 7 are the numbers of individual SPM; 14+16=Y2; Ob: 26+28+29=O1; 30+31=O2). The total weight of the samples was then between 25 and 55 mg. The same fractions were selected in the unified suspended sediment samples excluding a fraction >50 µm due to its very small part or its absence.

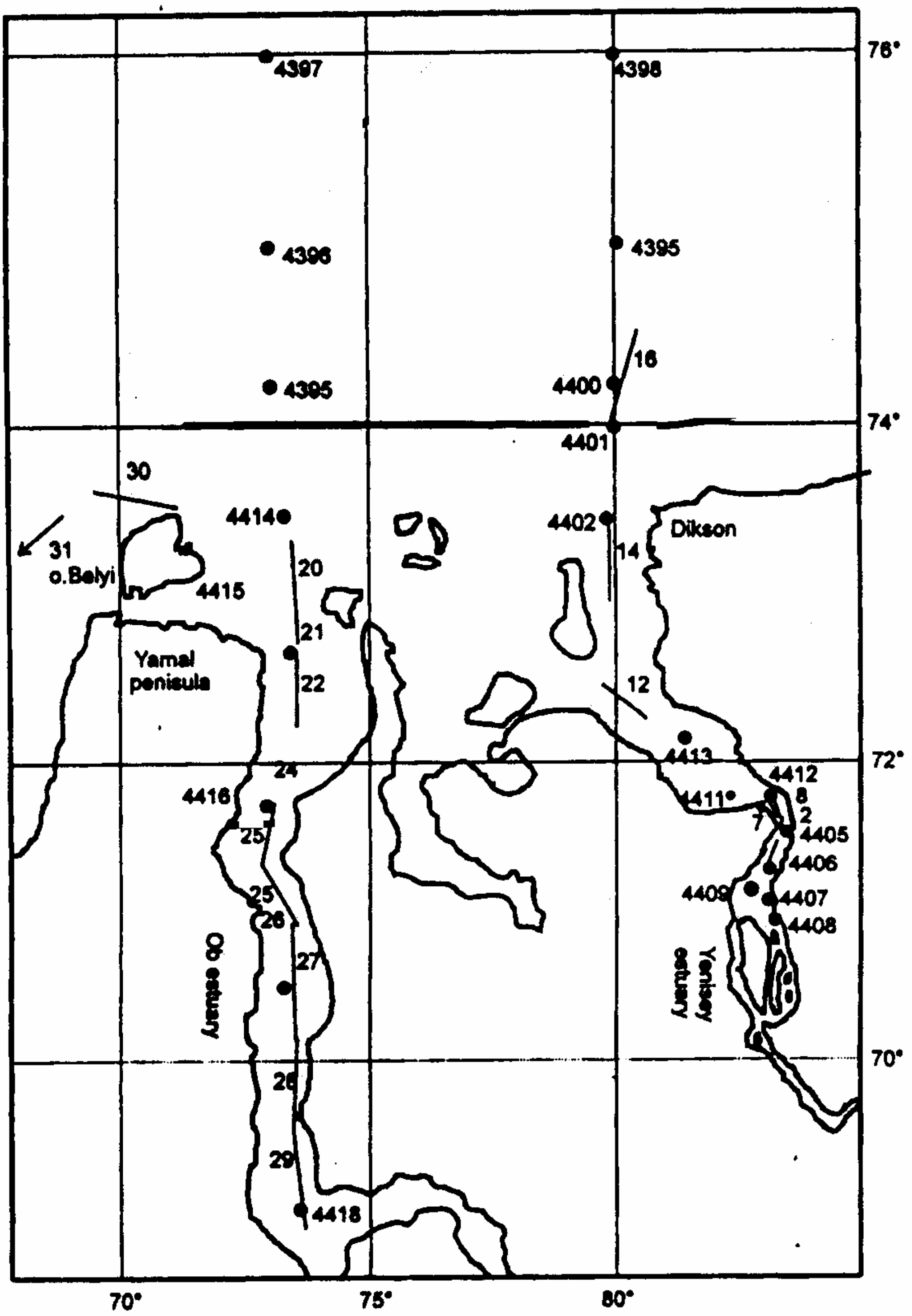

Figure 7 **Map of sampling locations of suspended matter (bars) and bottom sediment stations of the 49-th cruise of the R/V "Dmitry Mendeleev", 1993.**

The concentration of major elements (Si, Al, Ca, Mg, K, Na, Fe, Mn) in SPM were determined using a Perkin Elmer ICP 6000 inductively coupled plasma emission spectrometer. The trace element concentrations were measured with an Instrumentation-Laboratory IL 751 flame atomic absorption spectrophotometer (Cu, Zn) and with the Varian Spectr-AA3000 Zeeman graphite furnace spectrometer (Co, Cr, Ni, Pb). AAS and ICP analyses were carried out in the Laboratory of Chemical Oceanography of the Brussels University (Prof. R. Wollast - the chief of the laboratory).

Total digestion technique, using a mixture of $HCl+HNO_3+HF$ in Teflon bombs, heating in a microwave oven and subsequent addition of H_3BO_3, was applied to approximately 3-15 mg of suspended material and about 50 mg of bottom sediment samples. The reliability of the methods was tested with the certified standard material supplied by the Institute of Standards and Technology (Canada). The precision was < 5% for major elements and in a range 10-15% for trace elements (Paucot and Wollast, 1997).

The fractions of bottom sediments of station 4397, 4399 and 4417 and unified SPM (Y1 and Y2 -Yenisey, 01 and 02- Ob) were analyzed by instrumental neutron activation in the Vernadsky Institute of Chemistry and Analytical Chemistry in Moscow. The samples (2-20 mg) and reference rock-samples (TB, KH, SGD, SG - Germany, Russia) were subjected to radiation treatments by thermal-velocity neutrons of 2.8×10^{13} n/cm^2/sec. The gamma-radiation values were recorded on Ge and Ge - (Li) gamma-ray detectors (63 cm^3) connected with the multi-channel analyzers of impulses LP-4900 and NHC-8192, built on a computer-control base (ASPRO program).

The POC determinations were carried out by automatic titration using a Carbon express-analyzer AN-7529 (Gurvich et al., 1994).

3.2 28-th cruise of the R/V "Academic Boris Petrov" (1997)

The 28-th cruise of the R/V "Academic Boris Petrov" to the Kara Sea was conducted from August 21 to October 8 1997 in the framework of a joint Russian-German project (Futterer and Galimov, 1999). The project "The Nature of Continental Run-off from the Ob and Yenisey Rivers and its Behaviour in the adjacent Kara Sea" aimed at investigating the geological, biological and biogeochemical processes in the Ob and Yenisey Estuaries and in the adjacent Kara Sea. The station map is shown in Fig. 8.

Dissolved organic carbon (DOC) was analysed using a MQ 1001 TOC Analyzer, based on high-temperature catalytic oxidation. Potassium hydrogen phthalate dissolved in UV-treated Milli-Q water was used for calibration. International reference standards (44.0±1.5 µMC) were routinely analyzed and averaged 45.4± 1.4 µMC. The relative standard deviation at the 400-800 µM DOC level was 1-2%.

Total dissolved nitrogen was measured using a Technicon Autoanalyzer II system. Dissolved organic nitrogen (DON) was calculated by subtracting dissolved inorganic nitrogen from the total dissolved nitrogen. The relative error was about 5% (Amon and Spitzy, 1999; Kohler et al., 2003).

The concentration of NO_2, NO_3, NH_4, PO_4 and $Si(OH)_4$ was determined at the AWI using a Technicon Autoanalyzer II according to standard methods: NO_3 and NO_2 based on the method of Armstrong et al.(1967), NH_4 based on Koroleff (1969), PO_4 based on Eberlein and Kattner (1987), and silicate based on Grasshoff et al. (1983) and Nothig and Kattner (1999).

The chemical composition of SPM from Ob and Yenisey Estuaries was analyzed by XRF with the scanning spectrometer SPARK-1 and SPARK-2 at VNII Okeangeologia in St. Petersburg. Reference samples of oceanic bottom sediments (SDO-1, SDO-2, SDO-8, SDO-9) were used to control the accuracy of determinations (Lukashin et al., 1999). The error for major element (Si, Al, Ca, Fe, Ti) analysis is ± 3%, for trace element analysis (Ba, V, Cr, Mn, Co, Ni, Zn, As, Pb, Sr) up to 10%.

POC was determined by coloumetric method in the IO RAS, Moscow.

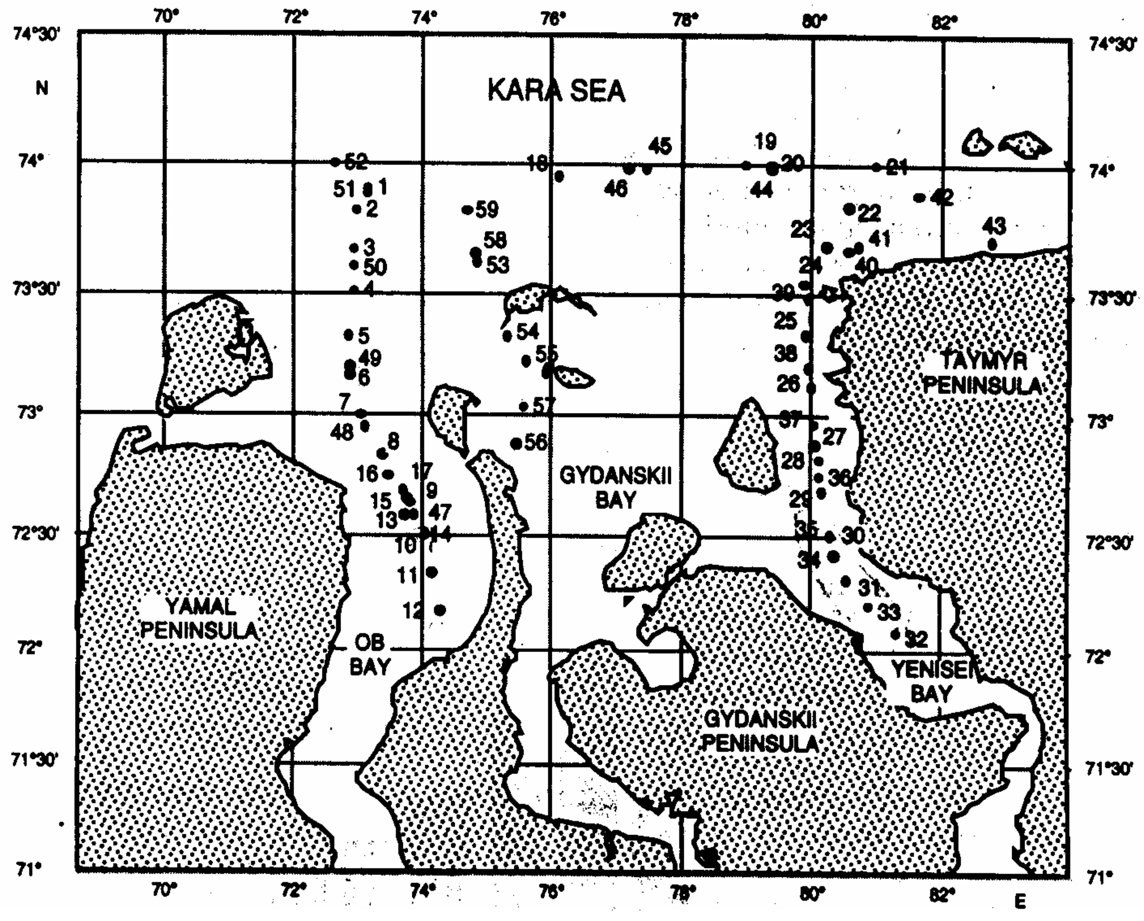

Figure 8 Sampling stations of the 28-th cruise of the R/V "Akademic Boris Petrov", 1997.

The chemical composition of bottom sediments was analyzed using the X-ray fluorescence spectrometer SPARK-1 (Krasnyuk and Vanshtein, 1999). Calculations of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Ba and Pb concentrations were performed by normalizing the data to the external standards. The statistical error of analyses was normally between 1 and 5%, and less than 30% for concentrations close to the detection limit.

Miroshnikov and Asadulin (1999) determined more than 25 chemical elements in bottom sediments by INAA in the Institute for Ore Deposits Geology, Mineralogy, Petrography and Geochemistry (IGEM) in Moscow. Samples and standards (BIL-1, BIL-2, RUS-4, KH, GM, TB, BM and SL-3) have been irradiated for 10 hours in neutron flux of 2.3x 10^{13} n/cm^2.sec.

Major and trace elements in surface bottom sediments of the Ob and Yenisey Estuaries and in the adjacent Kara Sea were determined also by Schoster and Stein (1999) using X-ray fluorescence spectrometry (PW 24000 and PW 14000 with Rh-tube, Philips). The results were checked with international reference standards GSR-5 (shale), “Alkaline Agpaite Granite” and the internal standards TW TUC (shale) and Loess (loess soil).

3.3 32-nd cruise of the R/V "Academic Boris Petrov" (1999)

A second expedition with the R/V “Acad. Boris Petrov” to the inner Kara Sea and to the Ob and Yenisey Estuaries took place from August 24 to September 8 1999 (Stein and Stepanets, 2000) (Fig. 9).

Sampling of water was conducted with Niskin bottles mounted to the CTD Rosette. SPM was obtained by filtering of water through pre-weighted Whatman GF/F glass fibre filters (Unger et al., 2001). Total carbon and nitrogen were measured using a Carlo Erba Nitrogen Analyzer 1500 (Unger et al., 2005). Nutrients (NO_2, NO_3, PO_4, DOP, total phosphorus (TP), Si) were analyzed by Sukhoruk and Tokarev (2001) on board ship.

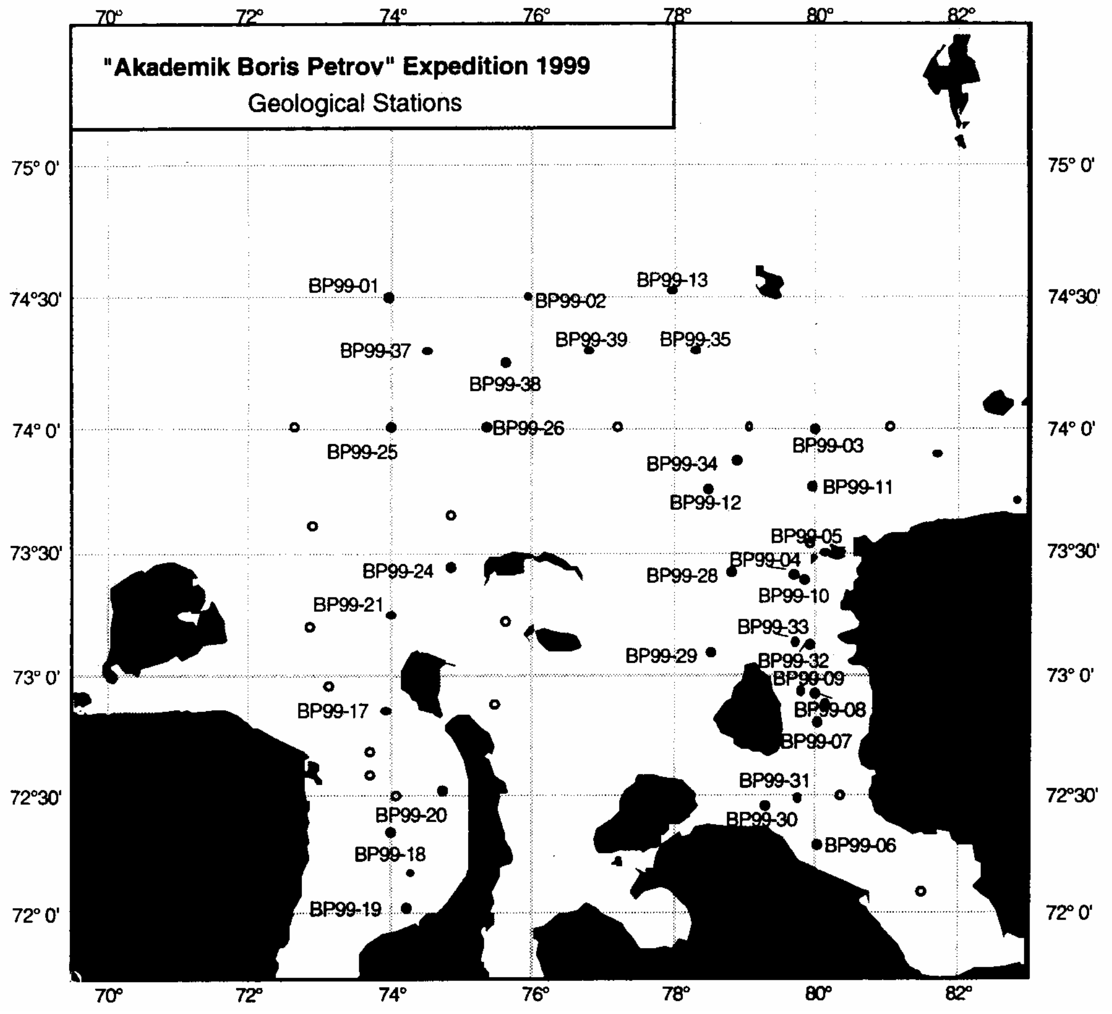

Figure 9 Sampling stations of the 32-nd cruise of the R/V "Akademik Boris Petrov" 1999; open circles are the stations of BP-1997.

3.4 35-th cruise of the R/V "Academic Boris Petrov" (2000)

The cruise was the third expedition within the joint Russian-German project SIRRO. The field work was carried out in August and September 2000 and concentrated on the SN transect from the Yenisey River towards the open Kara Sea between 70°N and 77°N. Main focus of this cruise was the investigation of geological, geochemical and biological processes relevant to the understanding of the freshwater and sediment input by the Yenisey River and the impact to the environments of the inner Kara Sea (Stein and Stepanets, 2001). During the expedition, an extensive sampling program was fulfilled on a total of 40 stations (Fig. 10). The methods of sampling and analyses were essentially the same as in the first two expeditions.

Dissolved major and minor elements (Na, Ca, K, Mg, Si, Fe, Mn, Sr, Ba) were determined by ICP-OES (Perkin Elmer, Optima 3000 XL), Cl, SO_4, Br and F were analyzed by Ion-Chromatography (Dionex, DX-320). The analytical precision was better than 97% for anions and 91% for cations. The accuracies were checked by parallel analyses of standard reference material (SRM 1634d, QCP 051) and range from 89 to 99% (Beeskow and Rachold, 2003). The hydrochemical parameters - total alkalinity, dissolved silica, inorganic phosphate, total and organic phosphorus, nitrate and nitrites have been analyzed without pre-filtration, immediately after sampling from the Rosette sampler (Methods …, 1978; Sukhoruk et al., 2001).

Total suspended material (TSM), POC and particulate nitrogen (PN) concentration were determined after filtration of water through Whatman GF/F glass fibre filters (Gebhardt et al., 2004; Unger et al, 2001).

The SPM-loaded filters were digested in HNO_3, HF and $HClO_4$ acids in PTEE autoclaves. Chemical elements in SPM samples (Al, Ti, Fe, Mn, Ca, Mg, K, Na, Ba, P, Cu, Ni, Sr, V and Zn) were analyzed by ICP-OES (Perkin Elmer, Optima 3000XL), As, Cd, Pb by ICP-AAS (Perkin Elmer, SIMMA 6000), Co, U, Y and REE by ICP-MS (Perkin Elmer, Sciex, ELAN 6000). The analytical precision for ICP-OES, GF-AAS and ICP-MS analyses was 3%, 8% and 11%, respectively. The analytical accuracies were checked by the analyses of the international reference standards GSD-9, GSD-11 and internal laboratory standards.

The grain-size distribution of selected SPM and bottom sediment samples was studied by laser-granulometry in a range from 0.2 to 1,000 μm by Coulter Electronics, LS-200 (Beeskow and Rachold, 2003).

The chemical composition of surface sediment was determined by instrumental neutron-activation analysis (Levitan et al., 2002) and by XRF using spectrometer SPARK-1 (Sizov et al., 2001).

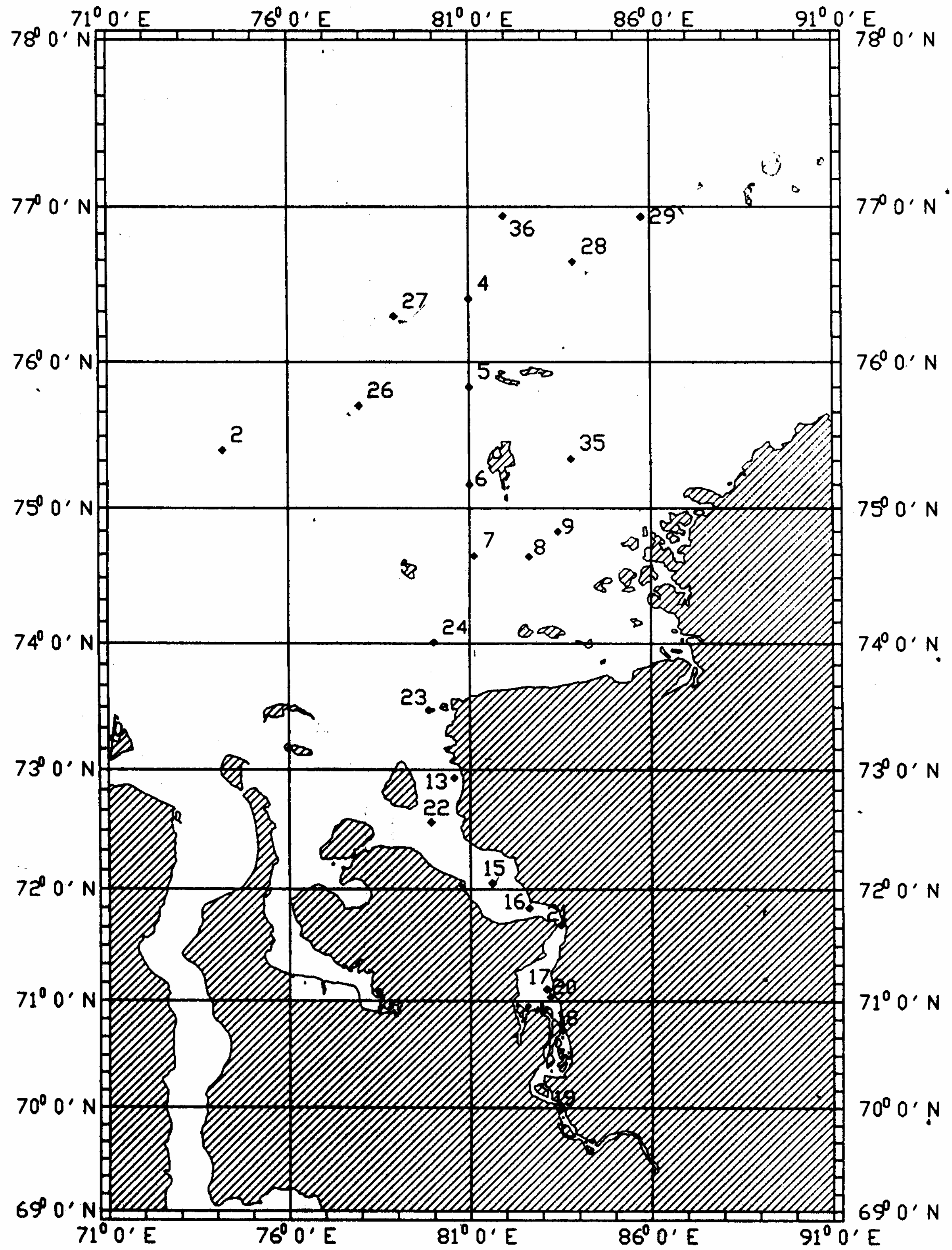

Figure 10 Sampling stations (hydrophysical and hydrochemical) of the 35-th cruise of the R/V "Akademic Boris Petrov", 2000.

3.5 36-th cruise of the R/V "Academic Boris Petrov" (2001)

This is a continuation of a series of expeditions since 1997. It was carried out in the Ob and Yenisey Estuaries and adjacent inner Kara Sea in August and September 2001 (Fig.11) (Stepanets and Stein, 2002; Stein and Stepanets, 2002).

Analyses of the chemical composition of water and SPM employed the same methods as in the previous expedition (Beeskow and Rachold, 2003). SPM concentrations, POC and PN were determined in the Institute for Biogeochemistry and Marine Chemistry, University of Hamburg, Germany (Gebhardt et al., 2002; Gebhardt et al., 2004), DOC and DON were determined in the same institute (Kohler et al., 2003). Dissolved inorganic nutrients (NO_2, NO_3, PO_4, SiO_4) were analyzed on board ship using filtered water samples (paper "blue-tape" filters, pore size of 1-1.5 μm) using standard methods (Methods …, 1978; Tokarev et al., 2003).

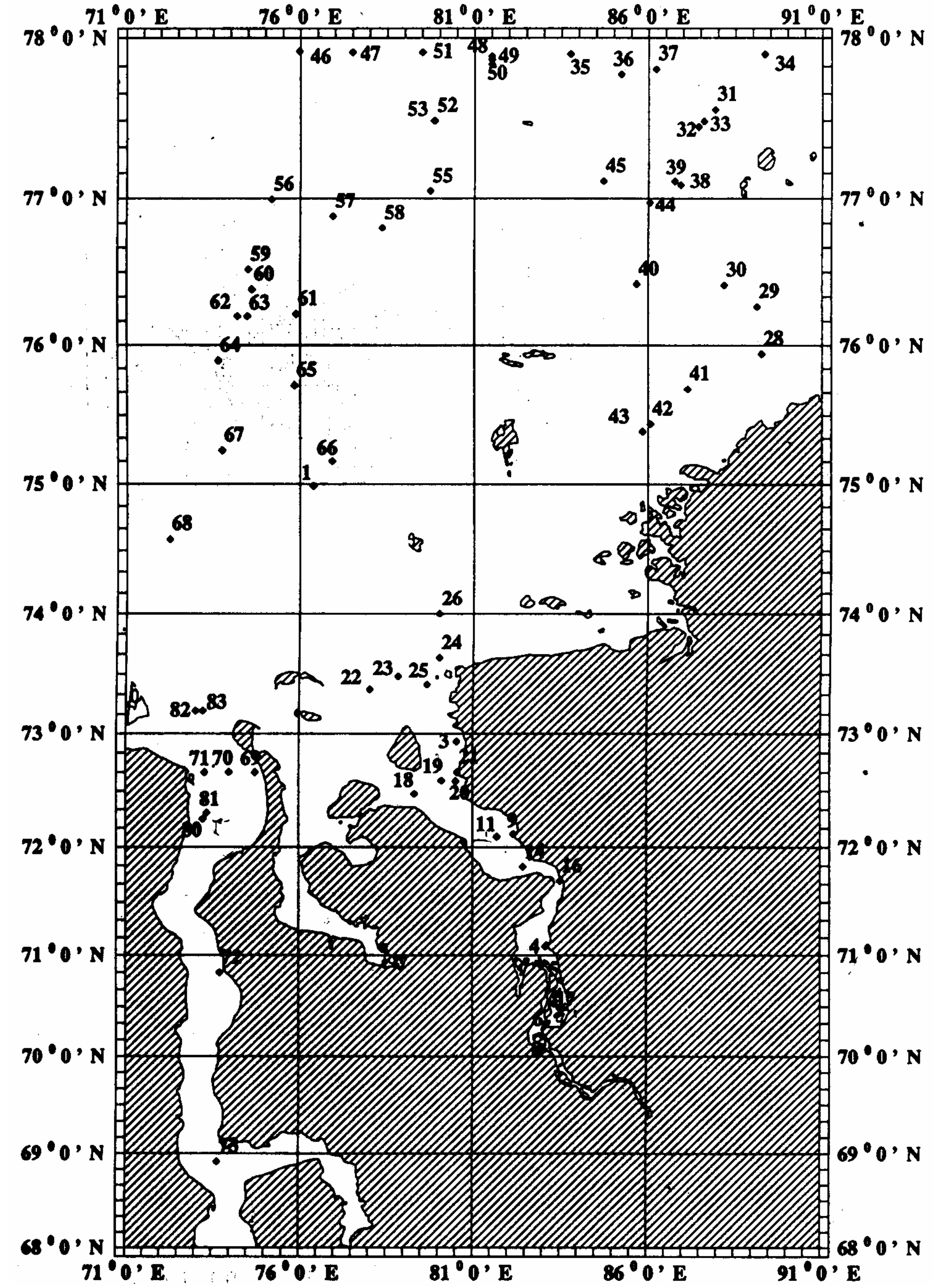

Figure 11 Sampling stations (hydrophysical and hydrochemical) of the 36-th cruise of the R/V "Akademic Boris Petrov", 2001.

3.6 38-th cruise of the R/V "Academic Boris Petrov" (2002)

The fifth expedition from 30th of September to 13th of October with the R/V "Academic Boris Petrov" focused on the inner Kara Sea and the Ob Estuary (Fig.12). The major nutrients and other hydrochemical parameters in river and sea water were published by Tokarev et al., (2003). Standard methods similar to that of earlier expeditions were used.

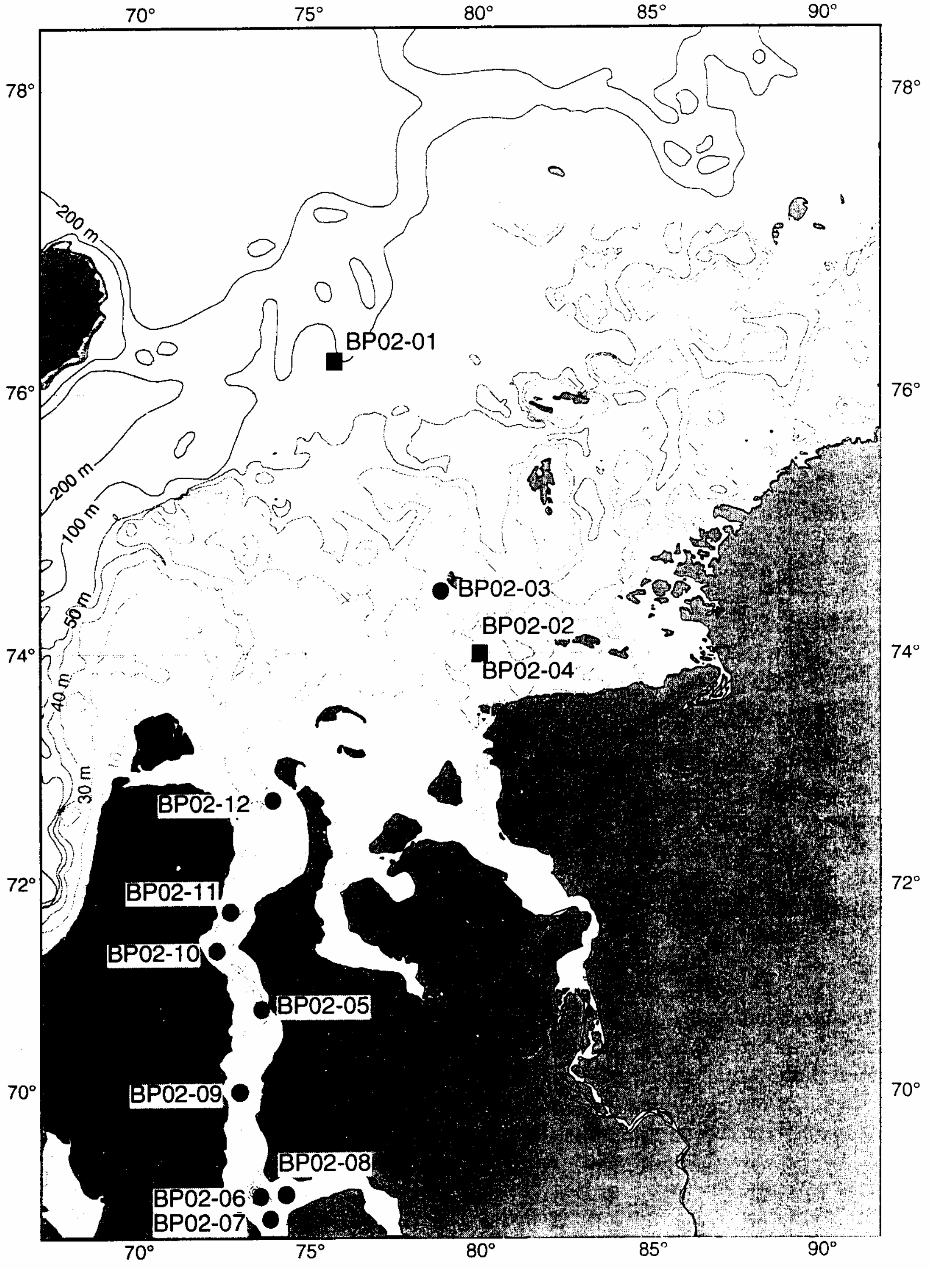

Figure 12 **Sampling stations and positions of sediment traps (BP02-01 and BP02-04) of the 38-th cruise of the R/V "Akademic Boris Petrov", 2002.**

3.7 39-th cruise of the R/V "Academic Boris Petrov" (2003)

The 39th expedition of the R/V “Academic Boris Petrov” was carried out in the framework of the Russian-German Program SIRRO in the Yenisey Estuary (8 stations) and in the adjacent Kara Sea in August 2003 (Fig.13). In this expedition only inorganic phosphates among nutrients were determined (Vlasova, 2004).

Figure 13 Sampling stations of the 39-th cruise of the R/V "Akademic Boris Petrov", 2003.

3.8 Expeditions to the delta and upper estuary of the Ob River (2000, 2001 and 2002)

Three small expeditions were carried out in the mouth of the Ob River (near Salekhard) and to upper estuary between 2000 and 2002 to obtain water and suspended matter.

The first expedition was focused on the Ob River near Salekhard (7-19 June 2000) and on the Yenisey River near Dudinka (23-29 June 2000). Specialists from the P.P. Shirshov Institute of Oceanology RAS in Moscow, the Hydrochemical Institute, Rostov on Don and The Ecosystem Center, Marine Biological Laboratory, Woods Hole, USA participated in the expedition. Water samples were collected along two transects across the Ob River (upstream and downstream of Salekhard) and along one transect across the Yenisey River near Igarka.

One aim of these expeditions was to measure dissolved inorganic nutrients in the same water samples by several methods. It was shown that the concentration of ammonium in Ob and Yenisey was significantly overestimated using the method of “Nesslerzation” which was accepted in the Unified Federal Service for Observation and Control of Environmental Pollution Network, Russia.

Methods and results used in the expedition are discussed in chapter 4.2.1.3.

The second expedition took place at the same location on the Ob River (Salekhard). Due to a deficit of geochemical data for the winter season, the expedition took place in December 2001 to obtain water and suspended sediment samples underneath the ice cover. Eight samples of Ob River water were collected on the section across the river 2 km upstream of Salekhard and 2 samples from the Polyi River, a tributary of the Ob River. On the Ob River, samples were collected near the surface in the polynias which were used permanently by the specialists of the local Hydrometeorological Station.

Water samples were poured into 10 l polyethylene cans. Filtration of samples and the determination of hydrochemical parameters and nutrients were carried out in the local laboratory in Salekhard 2-3 hours after sampling.

Filtration was done under vacuum through the nucleopore ultrafilters, 47 mm and 0.4 µm pore size (Obninsk, Russian) and glass-fibre filters GF/F for POC determinations. A closed plastic funnel Sartorius (Germany) was used to filtrate water for the determinations of dissolved metals. Filtered water was acidified with ultrapure HNO_3 up to pH=2 and stored in refrigerators in polyethylene bottles (100 ml).

The third expedition took place in period from 19th to 23th September 2002 and included 23 stations. Water samples were collected from the passenger ship "Mekhanic Kalashnikov" along its route from Salekhard to Antipayuta (the mouth of the Taz Guba) (Fig. 14).

Filtration of water samples through nucleopore and GF/F filters and determinations of temperature, pH, dissolved O_2 and NH_4 were made immediately on board ship.

Determinations of organic carbon, trace elements in SPM, dissolved nutrients were made by the same methods in both expeditions of 2001 and 2002. Dissolved Fe, Mn and Zn in river water (expedition of December 2001) were determined by flame atomic absorption (AA spectrophotometer "Quant-2A" from the firm "Kortek", Russia). Trace metals (Cu, Ni, Co, Cd, As, Cr) were measured by atomic absorption with the electrothermal atomizer GF-AAS (AA spectrophotometer "Quant-ZETA" from the firm "Kortek", Russia). To assess the accuracy of these determinations two reference samples of river and estuary, SLRS-4 and SLEW-3, of the National Research Council Canada were used.

Some major and trace elements contained in SPM were analyzed by ICP-OES (Perkin-Elmer, Optima 3000 XL), As, Cd and Pb by GF-AAS (Perkin-Elmer, SIMAA 6000) (Heinrich and Hermann, 1990). The methods are described in previous sections.

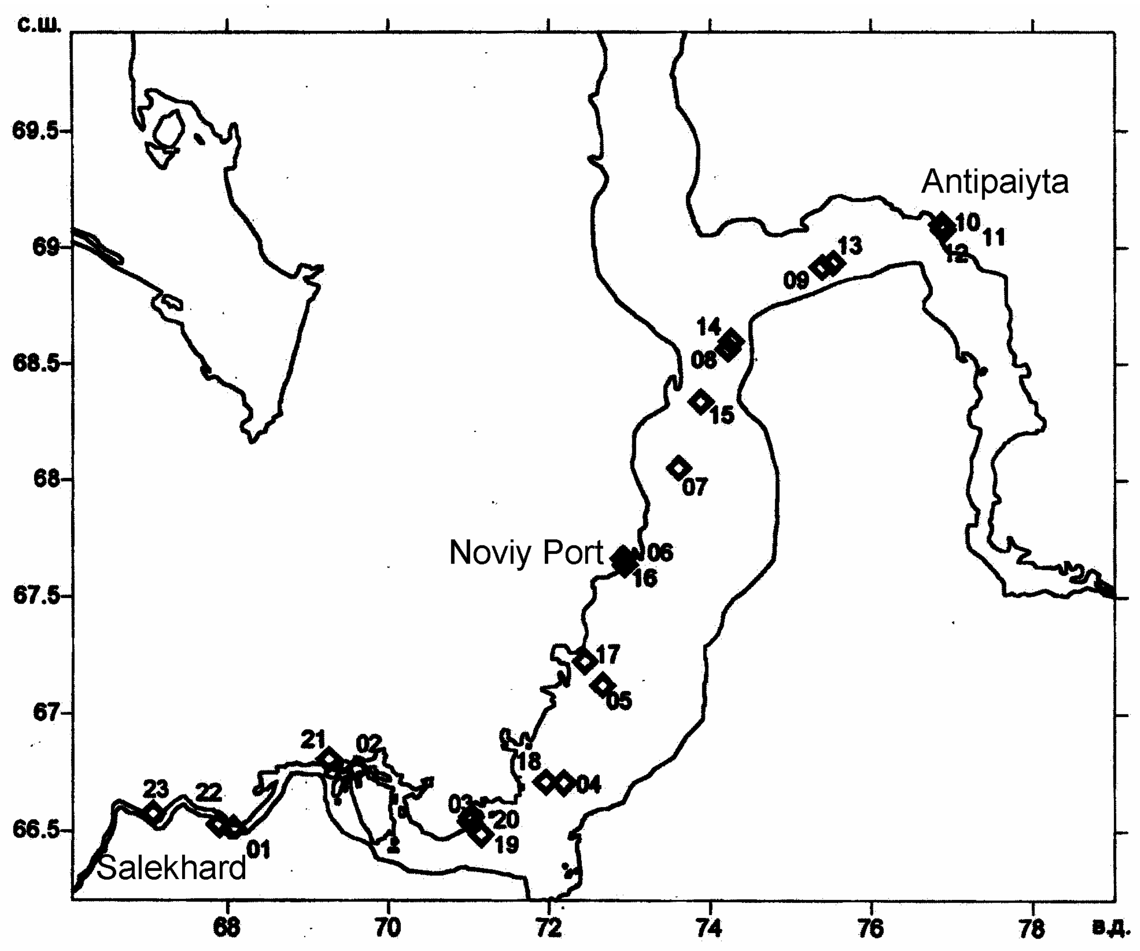

Figure 14 **Sampling stations of the Institute of Oceanology RAS expedition to the Ob mouth and estuary in September 2002 on board of the passenger ship "Mekhanic Kalashnikov".**

4 Results

4.1 River water, SPM and sediment discharge

Ob River

The Ob River and its tributaries drain an area of 2.54×10^6 km^2. Taking into account the endoreic (drainless) areas it is 2.95×10^6 km^2 (Bobrovitskaya et al., 2003). The average multi-annual water discharge is 404km^3/y (Gordeev, 2000). This is observed since 1936 at the Ob River outlet Salekhard. The analysis of water discharge variations depending on climatic (average air temperature, duration of ice cover) and anthropogenic factors has shown (Bobrovitskaya et al., 2003) that in the upper reach of the Ob River decrease of water discharge took place as a result of the dam constructions. However, in the lower course of the river (Salekhard) during the whole period of observations increase of discharge is about 5% only, from 389.2 km3/y at 30-th of last century to 410.3 km^3/y at present.

The variations of suspended matter discharge from 1960 to 1988 at gaging stations are shown in Fig. 15 (Meade et al., 2000) and from 1950 to 1995 at Salekhard in Fig.16 (Walling and Fang, 2003).

The observed decrease of SPM discharge in the upper basin for the last 30 years reflects the influence of the dams at Barnaul and Kolpashevo and on the Irtysh at Tobolsk. In Kolpachevo, the sediment discharge decreased from 16.2×10^6 t/y (1943-1973) to 7.2×10^6 t/y (1973-1993). However, the sediment discharge at Salekhard shows no statistically significant trend. At the same time, observations at Belogorie, about 700 km upstream of Salekhard, demonstrate an increase in SPM load from 19.2×10^6 t/y (1938-1956) to 28.4×10^6 t/y (1957-1990). This is due to a significant impact of human activity. Bobrovitskaya et al.(2003) considers that the wide flood plane, downstream of Belogorie, is one of the reasons for the constant sediment flux at Salekhard. A huge amount of sediments (about 59%) is deposited here and exchange between river and the flood plane.

The total sediment discharge of the Ob River is about 15.3×10^6 t/y (Bobrovitskaya et al., 2003) which practically coincides with the recent assessment by Holmes et al. (2002) of 15.5×10^6 t/y.

The seasonal variations of water and sediment discharge on 5 gaging stations on the Irtysh and the Ob River show that the month of greatest discharge shifts progressively down-river, from May at Omsk to June at Salekhard.

Yenisey River

The Yenisey catchment area covers a region of 2.59×10^6 km^2. Its multi-annual water discharge from the whole basin is 620 km^3/y (Gordeev, 2000) and near Igarka 581 km^3/y (Bobrovitskaya et al., 2003). As in the Ob basin, the observations of water discharge in Igarka have begun in 1936 while observations of sediment discharge have started in 1941.

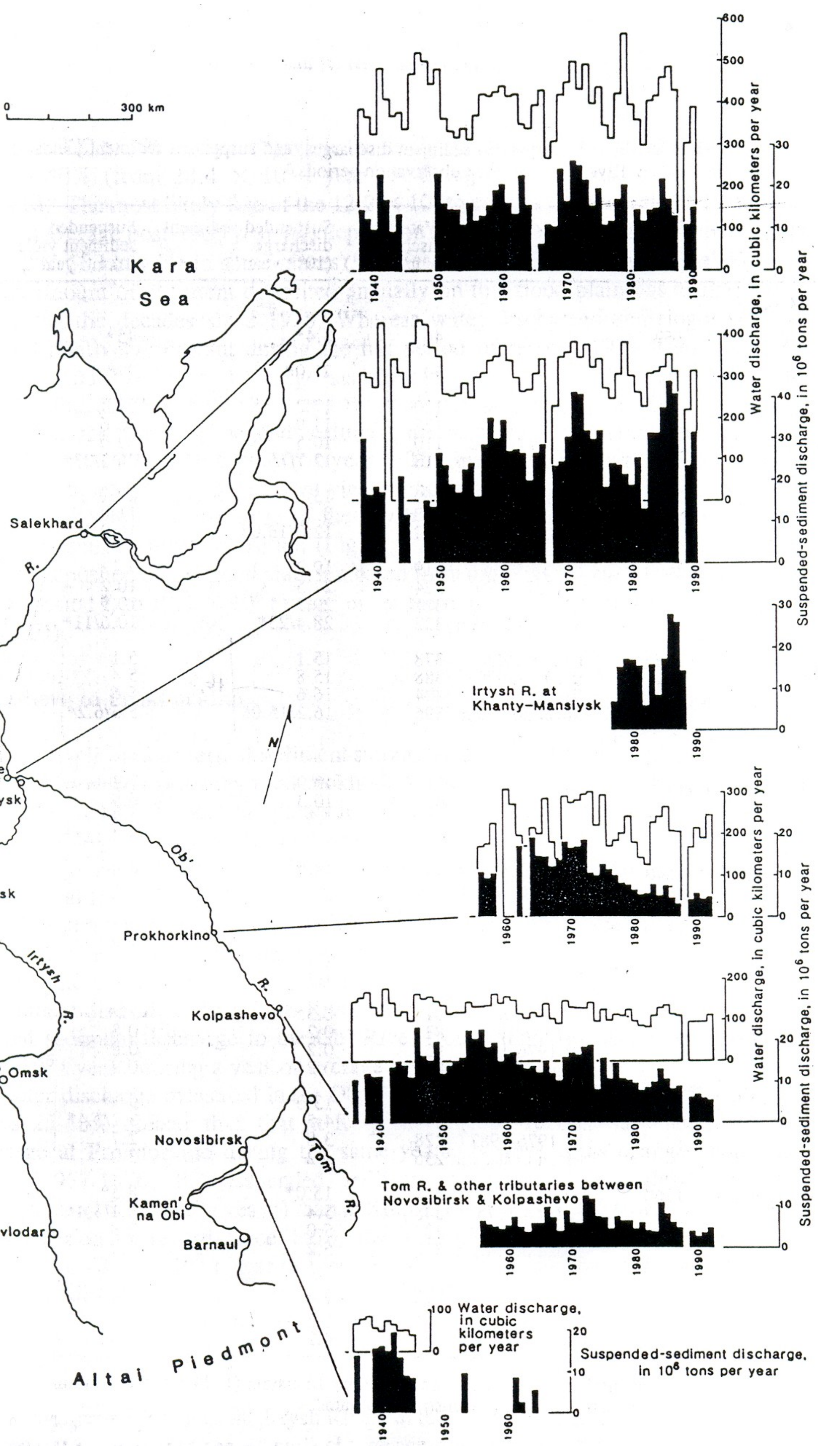

Figure 15 Suspended sediment and water discharges in the Ob River and selected tributaries, 1936-1992: annual sediment discharge shown as solid bars; annual water discharge shown as open bars (Meade et al., 2000).

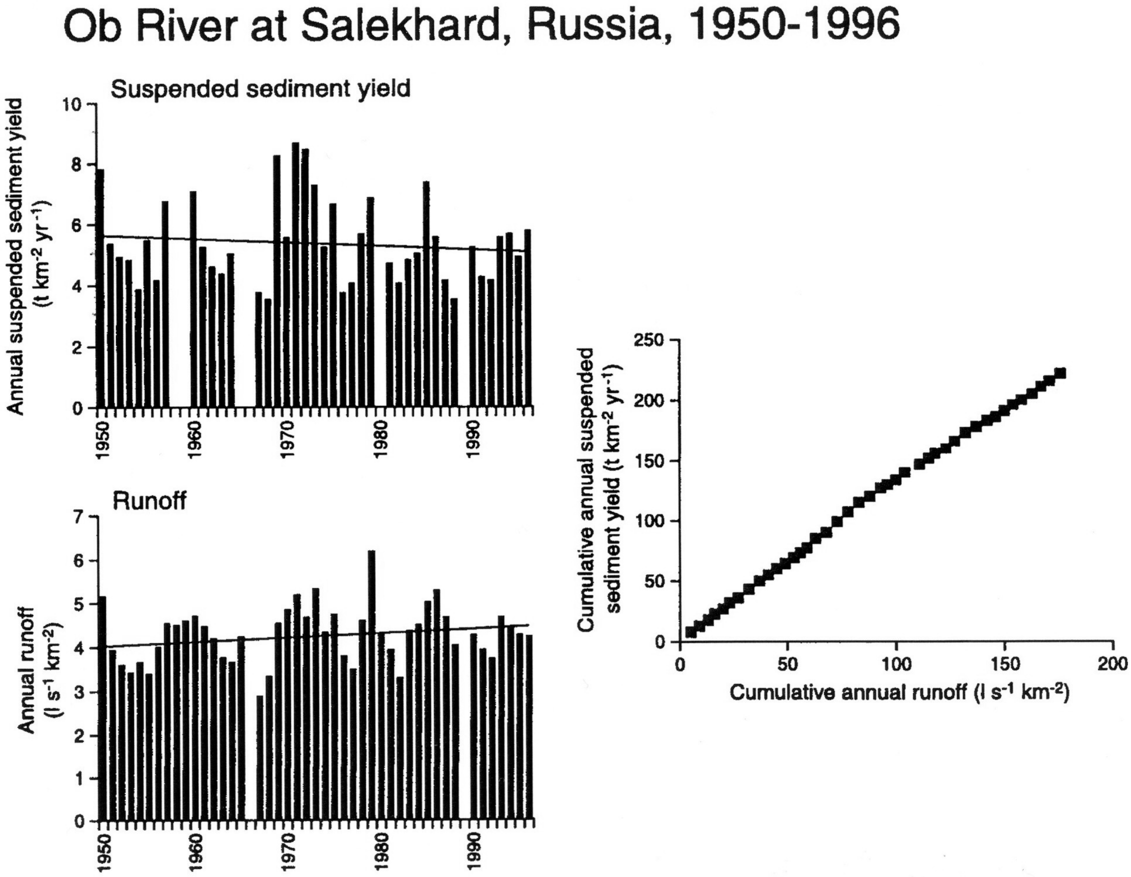

Figure 16 **Annual runoff and the sediment load of the Ob River at Salekhard in period 1950-1995. Double mass plot of cumulative suspended sediment yield versus cumulative annual water discharge emphasises the stable trend of the sediment flux relative to that of water discharge (Walling and Fang, 2003).**

Multi-annual variations of water and suspended matter discharge in the Yenisey basin are given in Fig.17. Bobrovitskaya et al. (2003) detected a small increase of water discharge near Igarka from 565.8 km^3/y to 590 km^3/y at recent time (i.e. about +4%).

The natural sediment flux in the Yenisey River before 1960 was 13.2×10^6 t/y (Milliman and Meade, 1983). The average modern multi-annual sediment flux near Igarka is according to Bobrovitskaya et al. (2003) about 5.6×10^6 t/y. Holmes et al. (2002) estimated 4.7×10^6 t/y.

The sediment flux decreased upstream of Krasnoyarsk for the last 30 years in natural limits from 1.46×10^6 t/y to 1.31×10^6 t/y. In 1967, a huge dam was completed on the Yenisey River near Krasnoyarsk and in 1970-s several additional dams were constructed along the Angara River, the main tributary of the Yenisey. After construction of the Krasnoyarsk Dam, the sediment discharge at Divnogorsk dropped from 6.3 to 0.2×10^6 t/y (Lisitzina, 1974).

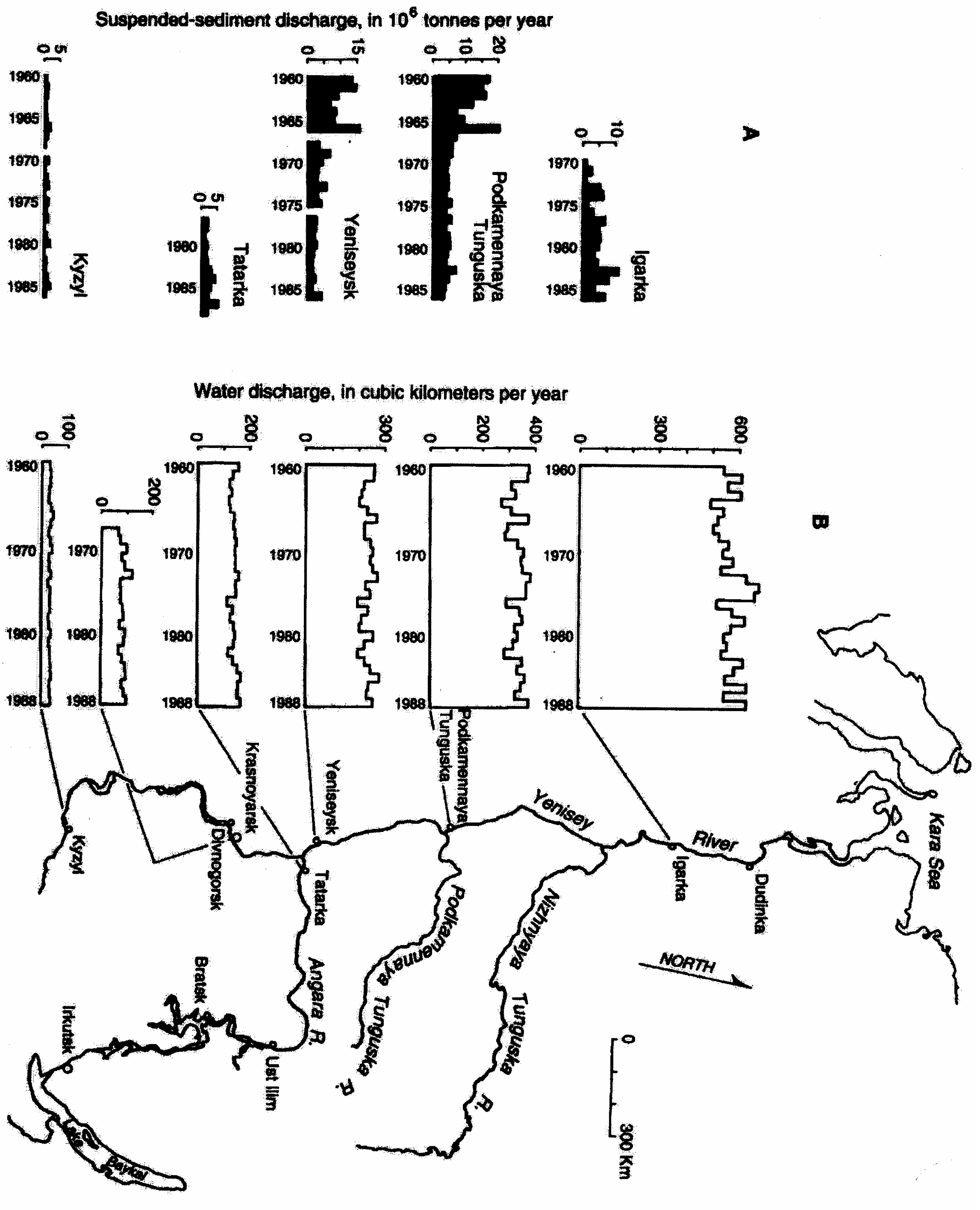

Figure 17 Annual discharges of suspended matter (A) and water (B) in the Yenisey River during period 1960-1988 (Meade et al., 2000).

4.2 Characteristics of Ob and Yenisey River end member

4.2.1 Dissolved load

4.2.1.1 Major ions

The average multi-annual concentration of major ions in the lower courses of Ob and Yenisey is given in Table 1[1] in comparison to the global averages. Also, the average concentration of cations and anions in the Ob Guba (S=0 ‰, n=8) and in the Yenisey Bay (S=0 ‰, n=16) during the 36-th cruise of the R/V "Academic Boris Petrov" in 2001 is presented. The average concentrations of major ions of Ob and Yenisey water are very similar (100-120 mg/l) and only slightly above the global average (Table 1).

The main type of waters is the hydrocarbonate one with domination of Ca+Mg over Na+K (Fig. 18 A).

On the triangular Ca-Mg-(Na+K) diagram Ob and Yenisey are located in the bottom left-hand corner together with points presenting water of Lena, Mackenzie, Yukon, Ganga-Brahmaputra and the average value for all world rivers. On the triangular diagram for SiO_2-HCO_3-(Cl+SO_4) the typical carbonate water (Ob, Yenisey, Lena, Mackenzie, Ganga, Huang He, Yangtze and average for the world rivers) are located at the top of the diagram (Fig. 18 B) whilst river where weathering of the silicate rocks predominates (Amazon, Congo, Orinoco) concentrate in the bottom left-corner.

No data on seasonal variations of major ions in Ob and Yenisey are available. It is likely that these variations are similar to that of the Lena River (Fig.19). One can see that at winter’s time, when the water discharge is minimum, the waters of the Lena River have a maximum in a year mineralization and high concentrations of all major ions. At peak time in June when maximum discharge exceeds minimum discharge almost 60 times, mineralization decreases in 4 times and ion concentrations decrease to minimum value also due to high dilution of river water by snow water of very low mineralization.

Variations of water discharge in Ob and Yenisey are very similar to that of the Lena. Therefore, lower major ion concentrations and the sum of dissolved salts in the Ob in September 2001 (Table 1) are probably related to seasonal variations as well as the Yenisey waters at August 2001.

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[1] Notice: Tables 1-43 are presented in the Annex, pages 196 ff.

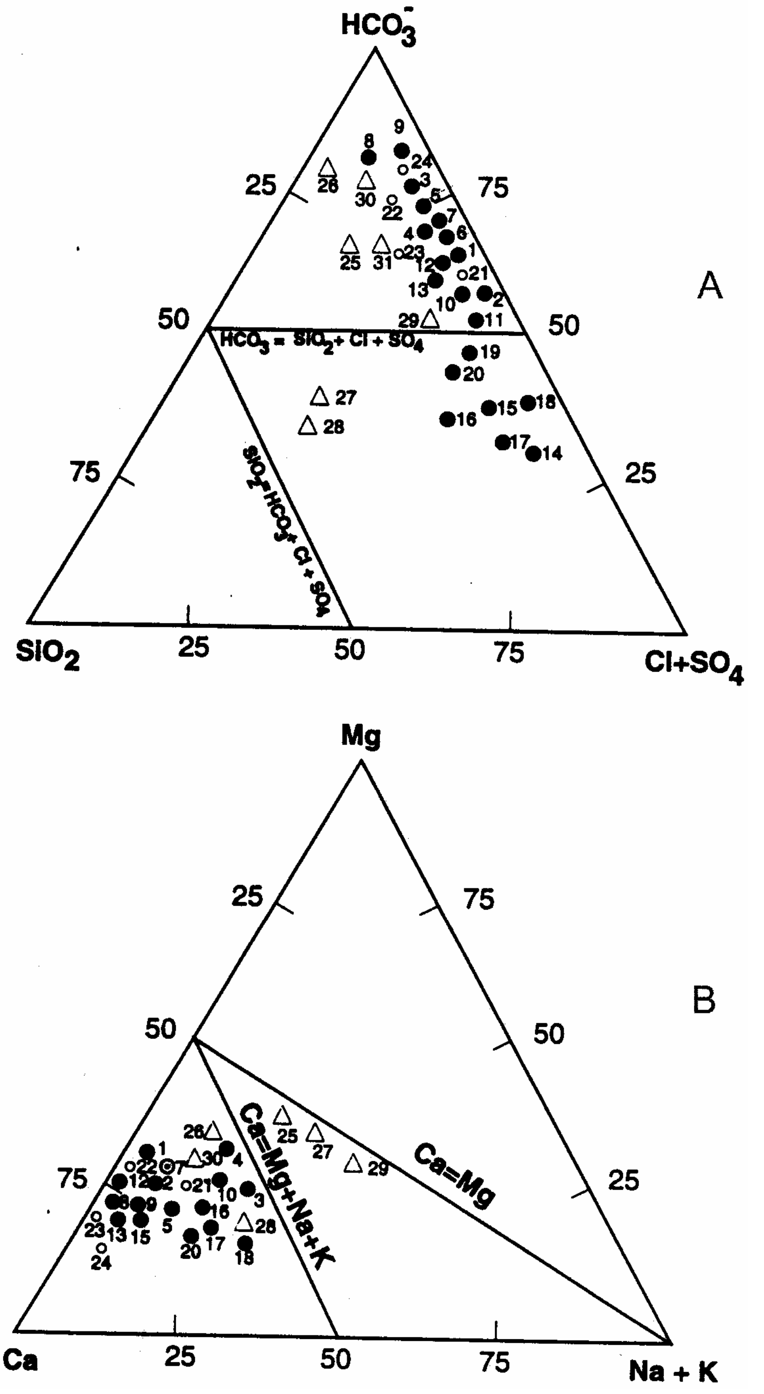


Figure 18 Triangular diagrams of dependence HCO_3 - ($CL+SO_4$) - SiO_2(A) and Mg - Ca - (Na+K) (B) for the main Arctic rivers and some big rivers from other climatic zones (Gordeev et al., 1996). Rivers of the Russian Arctic: 1 - Onega, 2 - N. Dvina, 3 - Mezen, 4 - Pechora, 5 - Ob, 6 - Yenisey, 7 - Khatanga, 8 - Anabar, 9 - Olenjok, 10 - Lena, 11 - Yana, 12 - Indigirka, 13 - Kolyma; middle and small basin of the East - Siberian Sea, 16 - the basin of the Chukchi Sea; 17 - Omoloi, 18 - Ebitem, 19 - Alazeya, 20 - Amguema; North American Arctic rivers: 23 - Kobuk, 24 - Kuparuk; the greatest World rivers; 25 - Amazon, 26 - Gang - Brahmaputra, 27 - Congo, 28 - Orinoco, 29 – Huang He, 30 - Yangtze; 31 - average for the global rivers; I - Eurasian rivers (1-20), II - North American rivers (21-24); III - the largest World rivers (25-31).

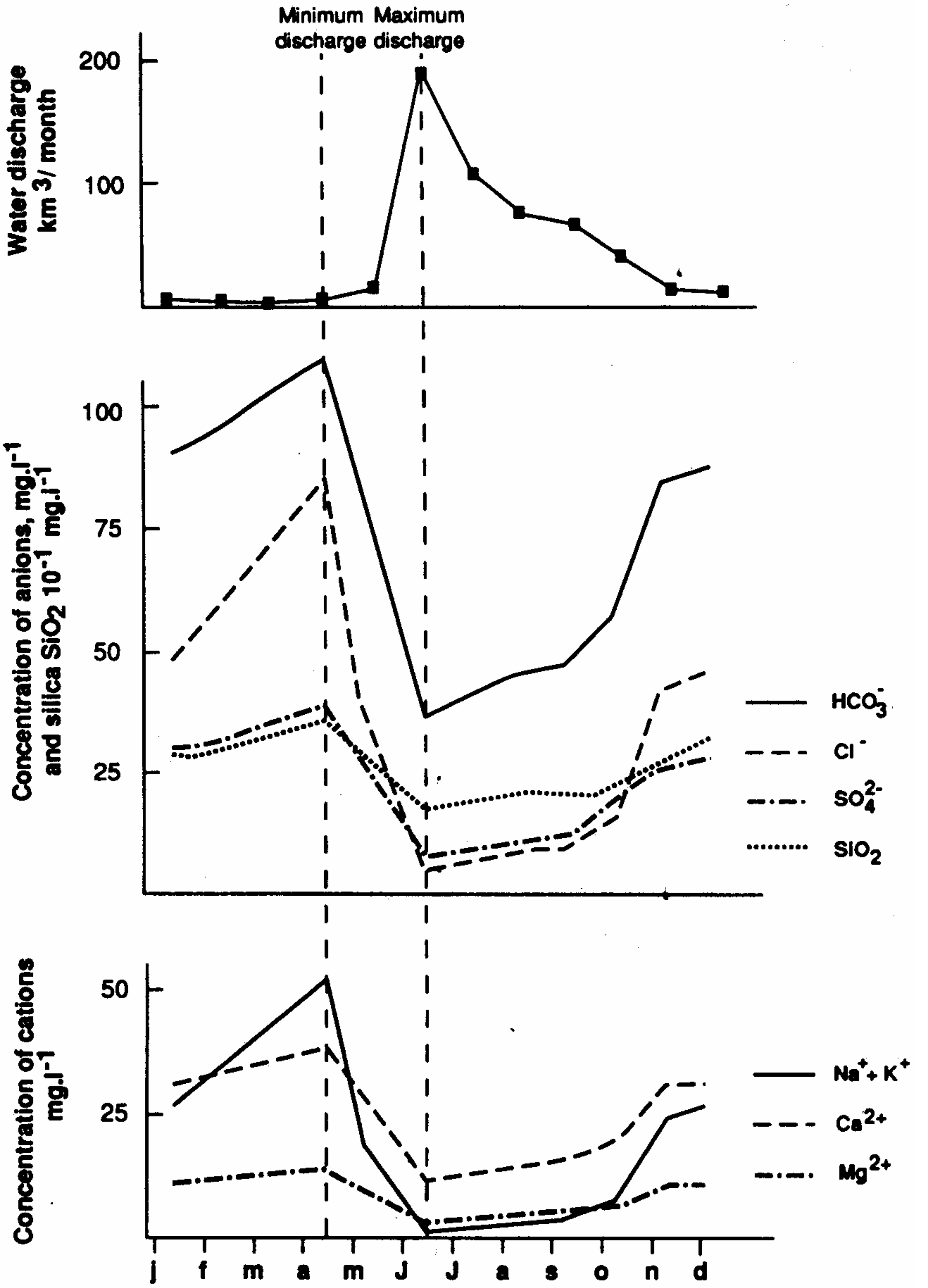


Figure 19 Seasonal variability of water discharge and major ion concentrations in the Lena River (average for period 1975-1990) (Gordeev and Sidorov, 1993).

4.2.1.2 Dissolved organic carbon (DOC)

A summary of published data on DOC in Ob and Yenisey is given in Table 2. Ludwig and Probst (1996) established empirical relationships between DOC fluxes and various factors characterizing the catchment area of the rivers. According to their model, DOC concentrations increase with flatter morphologies and larger carbon reservoirs in the soils of the drainage basins. It means that higher DOC concentrations for the Ob than for the Yenisey would be expected. Dai and Martin (1995) have reported higher DOC concentrations in the Ob bay at zero salinity (7.2-10.0 mg/l relative to the Yenisey with 3.6-4.2 mg/l during the 49-th cruise of the R/V "Dmitry Mendeleev" in 1993). But the data by Kohler et al. (2003) (fieldwork was carried out in the framework of the joint Russian-German project SIRRO during 3 cruises of the R/V "Academic Boris Petrov" in August-September 1997, 1999 and 2000, plus additional sampling in June 2000 near Salekhard during a land-based expedition to the Ob River (Holmes et al., 2001)) have shown that the DOC concentrations in the Ob (4.3-11.3 mg/l, av. 7.7) were comparable with the Yenisey (6.7-8.4 mg/l, av. 8.2). A possible explanation for lower DOC values in the Ob bay might be the large volume of the Ob bay due to its morphology (Kohler et al., 2003). Fig. 20 shows the DOC distribution across the Ob River upstream of Salekhard in June 2000. The DOC difference within the cross-section profile was relatively small, within a range of 869 to 939 μM (or 6.2-6.7 mg/l).

Seasonal variations of DOC concentration in Ob and Yenisey are shown in Fig. 21 A and B. The highest DOC concentrations with more than 10 mg/l were detected in June at peak flood and concentrations are low in winter when rivers are predominantly fed by groundwater with low carbon content. During spring flood in May and June the DOC concentrations reach maximum values due to the export of organic matter which was accumulated in soils during winter time.

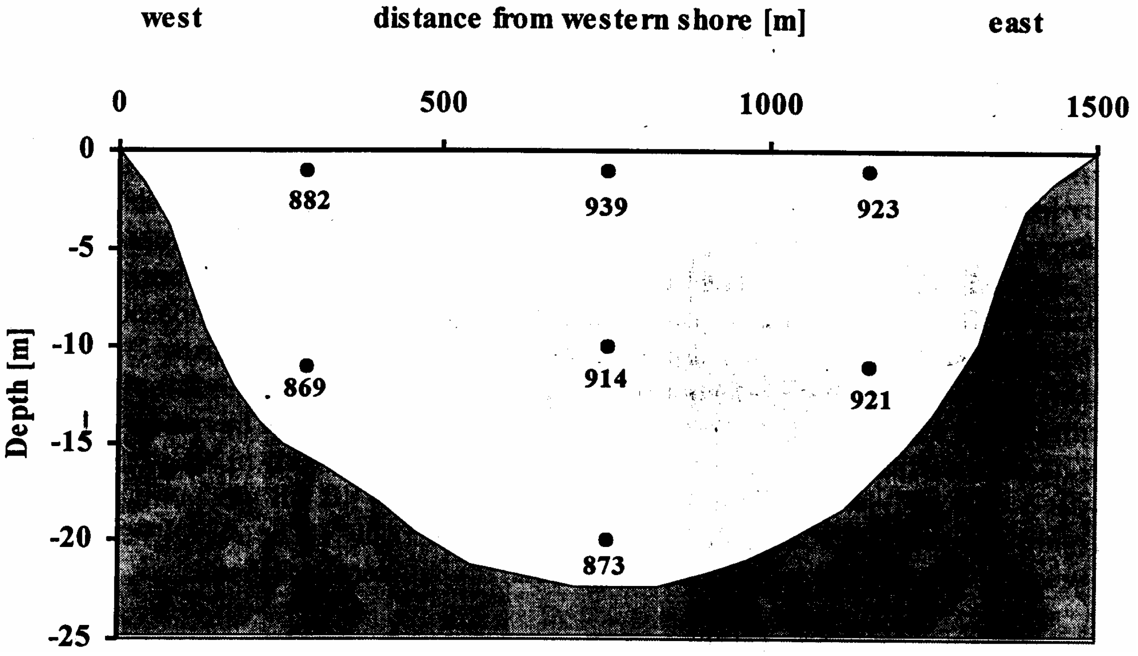


Figure 20 DOC distribution (in μM) in the cross-section of the Ob River upstream Salekhard in June 2000 (Kohler et al., 2003).

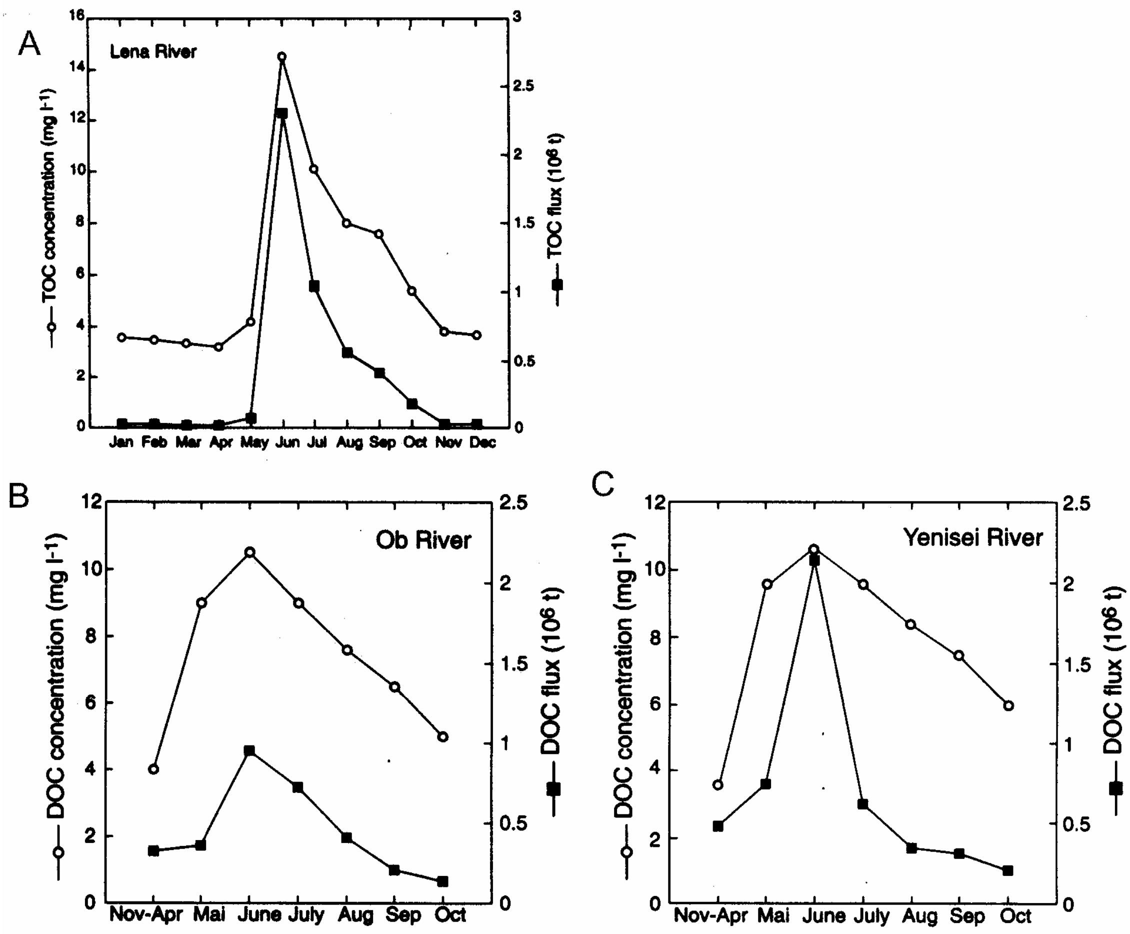


Figure 21 Seasonal variations of DOC concentrations and fluxes of the Ob (A) and Yenisey (B) Rivers (Kohler et al., 2003) and of TOC concentrations and fluxes in the lower reaches of the Lena River (C) (Cauwet and Sidorov, 1996).

4.2.1.3 Nutrients

Dissolved nitrogen, phosphorus and silicate belong to the group of nutrients. Related to silica, no generally adopted relation exists to this element as to the nutrient element. Because it is not a place to discuss this question we include silica in consideration in this section.

Nutrient concentration in Ob and Yenisey is (except for NH_4) generally low (Table 3). NO_3 and Si in both rivers are lower compared to the global average; the PO_4 concentration of the Ob is higher than the global average. The nutrient concentration in the Ob is generally higher than that of the Yenisey.

In the 90s of the last century a group of Russian and American specialists have summarized the data of the Hydrometeorological Survey for period from 1970 to 1995. The average multi-annual concentrations of nitrates, ammonium and phosphates, their monthly averages and annual fluxes for 15 large Siberian rivers were calculated by Holmes et al., 2000. The assessment of the annual flux of NH_4 in Ob and Yenisey has shown that it is 2-2.5-fold higher than that of the World biggest river Amazon River which a water discharge is one order higher than that of Ob and Yenisey. Furthermore, the NH_4 concentration in all 15 Siberian rivers is higher than the sum of all other inorganic forms of nitrogen while normally nitrates are prevailed in river waters. The question arises - are the Siberian rivers really unique on their hydrochemical role in the nitrogen global cycle, or are the available data on NH_4 strongly overestimated?

To answer this question a special expedition to the mouth areas of Ob and Yenisey was organized with participation of Russian and American specialists (Holmes et al., 2001; Makkaveev and Holmes, 2001; Makkaveev et al., 2002). Water samples were collected in Ob (Salekhard) and Yenisey Rivers (Dudinka) and analysed for NH_4, NO_3 and PO_4 in laboratories of the Marine Biological Laboratory, Woods Hole, USA, in the P.P. Shirshov Institute of Oceanology, Moscow and the Hydrochemical Institute in Rostov on Don, and by the local group of the Hydrometeorological Survey of Russia. The results are given in Tables 4 and 5 and show that the NH_4 concentration measured by the local laboratory is essentially higher in comparison to results of the other laboratories. The concentration of the other nutrients, however, is similar in all laboratories. The overestimation of the NH_4 concentration is likely to be caused by the used method of "Nesslerezation" which is unsuitable for the analysis of waters with high level of organic and suspended sediment substances. Therefore, the numerous multi-annual data on NH_4 concentration in the Russian Arctic rivers and, based on them, the estimates of ammonium fluxes into the Arctic Ocean are not reliable (Gordeev et al., 1996). Because the overestimation has irregular character and is different in the Siberian rivers, it is not possible to introduce a coefficient for data correction but a new, reliable analysis method of NH_4 concentration and its fluxes in the Arctic rivers needs to be established.

Fig. 22 and 23 show the distribution of dissolved inorganic N, P, Si and O_2 along cross-sections through Ob and Yenisey in June 2000, upstream and downstream of Salekhard, and upstream of Dudinka respectively. Significant irregularities of hydrochemical parameters were found in the vertical distribution, and also on the cross-sections despite of high water currents in both rivers. It means that the water inflow to the main channel from different areas of the watersheds kept their characteristics for a long time.

It is a well-known fact that the major fraction of riverine nitrogen is organic one (Meybeck, 1982). A compilation of available DON concentration and the C/N ratios for DOM in the Arctic river and other aquatic environments of the Arctic is presented in Table 6.

Dissolved inorganic nitrogen (NO_2, NO_3, NH_4) in surface samples is low with a mean of 1.5 µMN whilst DON values range from 5 to 15 µMN, with an average of 8 µMN in the Kara Sea and a maximum of 15µMN in the Yenisey River. There are some discrepancy in DON data reported for the Arctic rivers and adjacent shelf seas. In most cases DON is calculated as the difference between total dissolved nitrogen (TDN) and the sum of inorganic nitrogen (NO_2, NO_3 and NH_4). Taking into account the erroneous results on NH_4 concentrations in the Arctic rivers there may be similar problems with respect to the DON data.

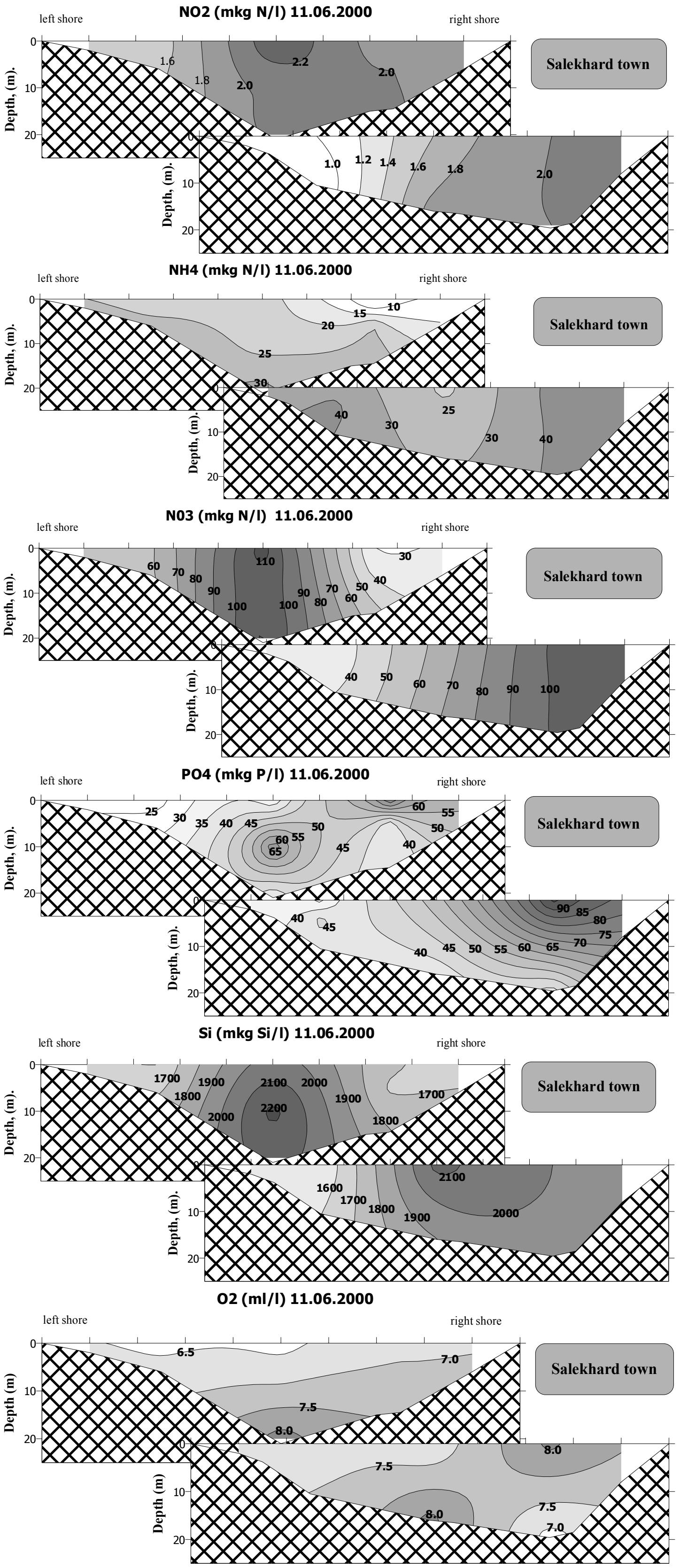


Figure 22A Distribution of dissolved oxygen (ml/l), silicate (µg Si/l), phosphate (µg P/l), nitrate, ammonium and nitrite (µg N/l) in the Ob water upstream and downstream of Salekhard (11 June, 2000) (Makkaveev et al., 2001).

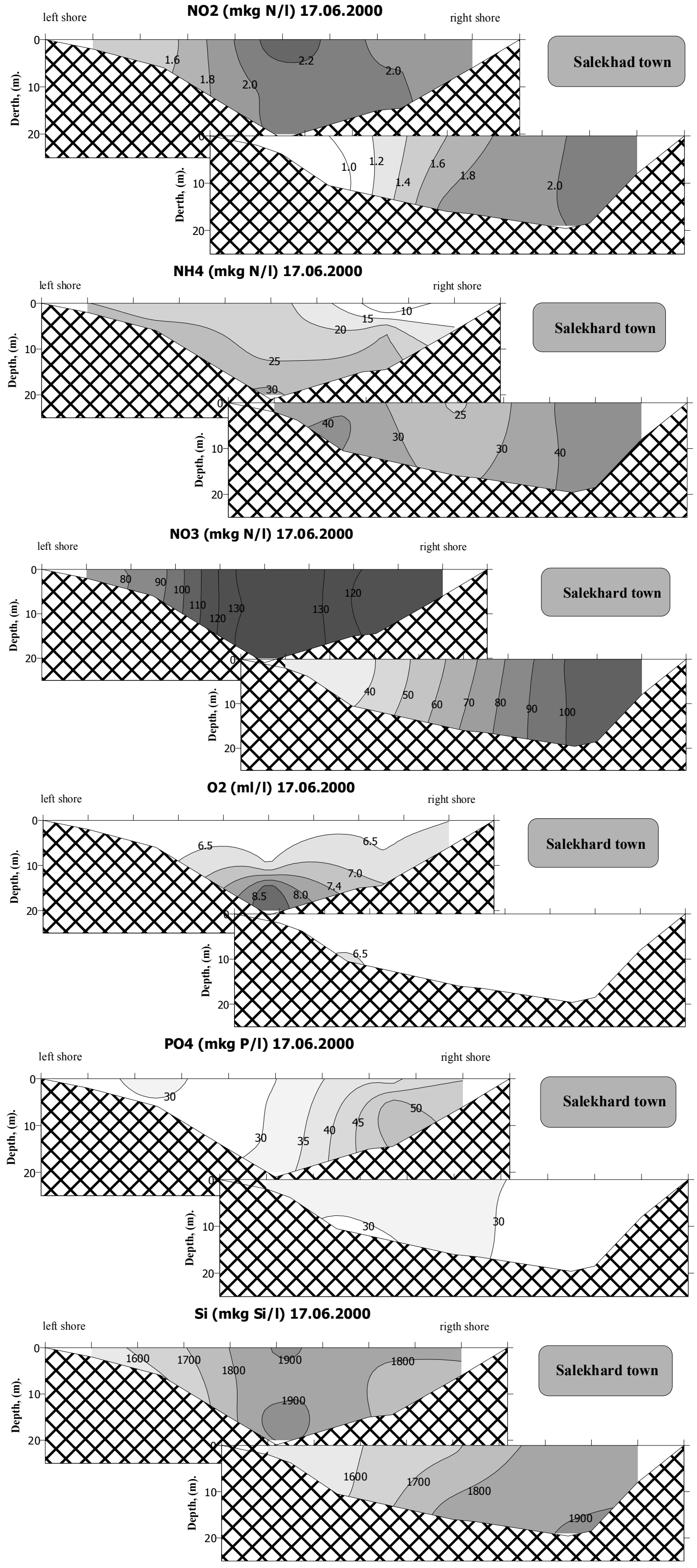


Figure 22B Distribution of dissolved oxygen (ml/l), silicate (µg Si/l), phosphate (µg P/l), nitrate, ammonium and nitrite (µg N/l) in the Ob water upstream and downstream of Salekhard (17 June, 2000) (Makkaveev et al., 2001).

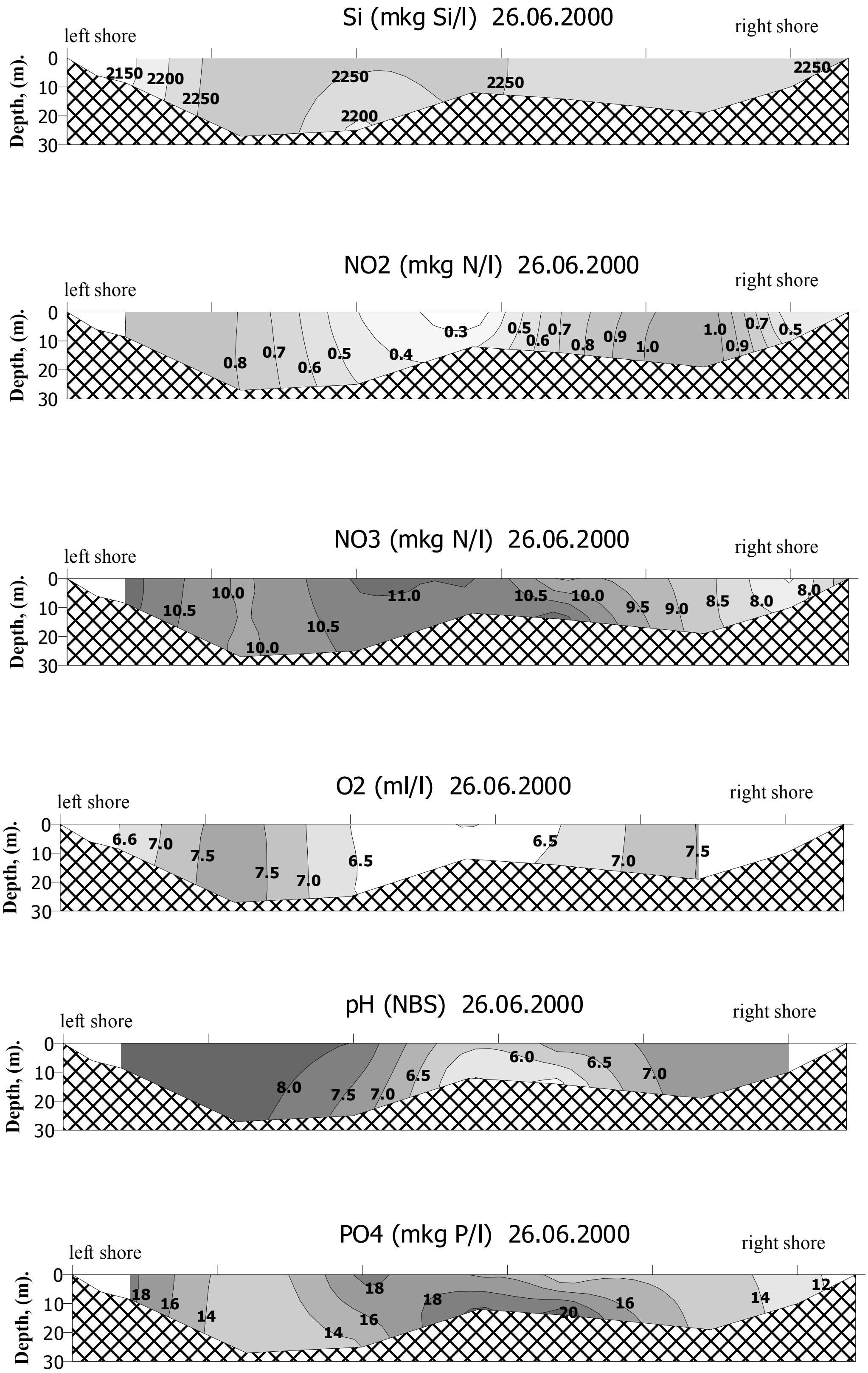


Figure 23 Distribution of dissolved oxygen (ml/l), pH (NBS), phosphate (µg P/l), silicate (µg Si/l), nitrate and nitrite (µg N/l) in the Yenisey waters near Dudinka (June 26, 2000) (Makkaveev et al., 2001).

The data obtained in December 2001in the Ob River are shown in Fig. 24 together with data from June 2000. Only the phosphate concentration is similar in winter and summer. All other nutrients, however, are significantly higher in winter's time.

The increase of the SiO_2 concentration from 65 µM in summer to 128 µM in winter indicates a change of water sources in the river from surface to underground ones. NO_3 concentration increases approximately 2 times, and NH_4 more than 4 times. These changes of inorganic nitrogen are not only to explain by a weakening of the assimilation by photosynthesis and by prevailing of the oxidation processes. A part of the effect may be related to a change in composition of water inflow into the river (Makkaveev et al., 2002).

In winter, significant heterogeneities in nutrient distribution along river cross-sections are retained. Despite high river currents a total mixing of water and a smoothing of hydrochemical parameters does not occur for a long distance from the location of water input to the river.

Fig.24-a

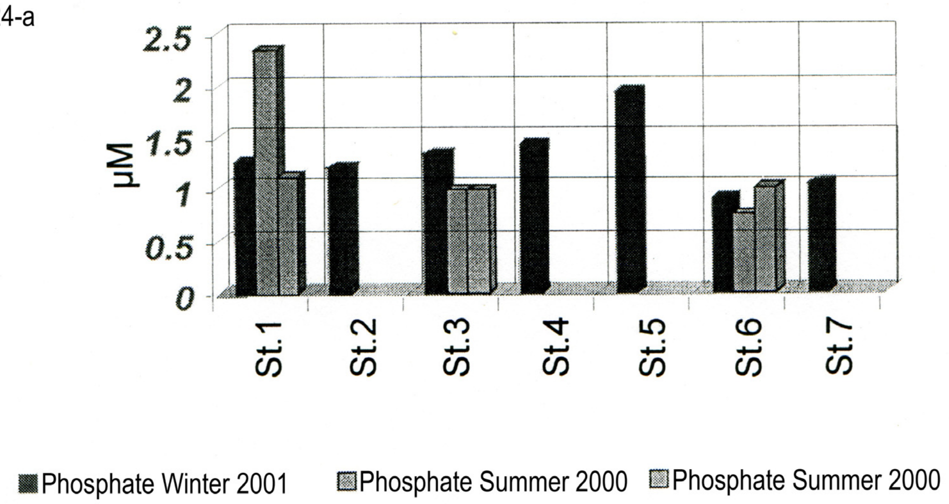


Fig.24-b

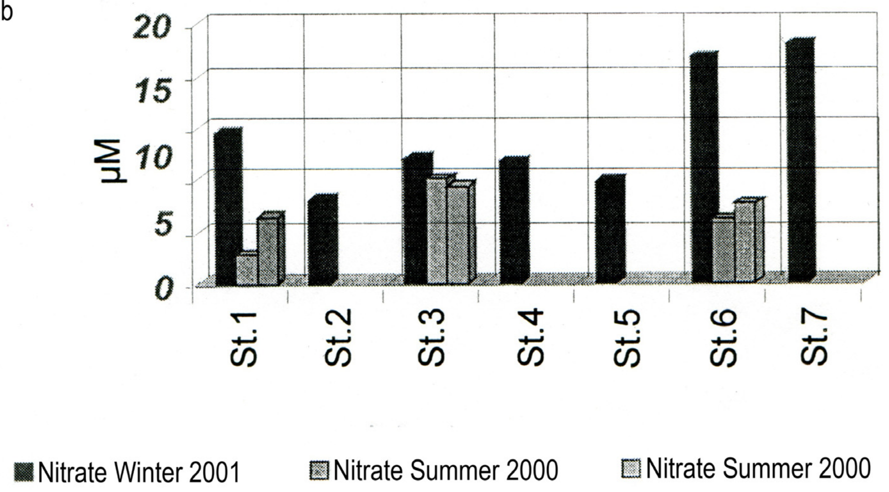


Fig.24-c

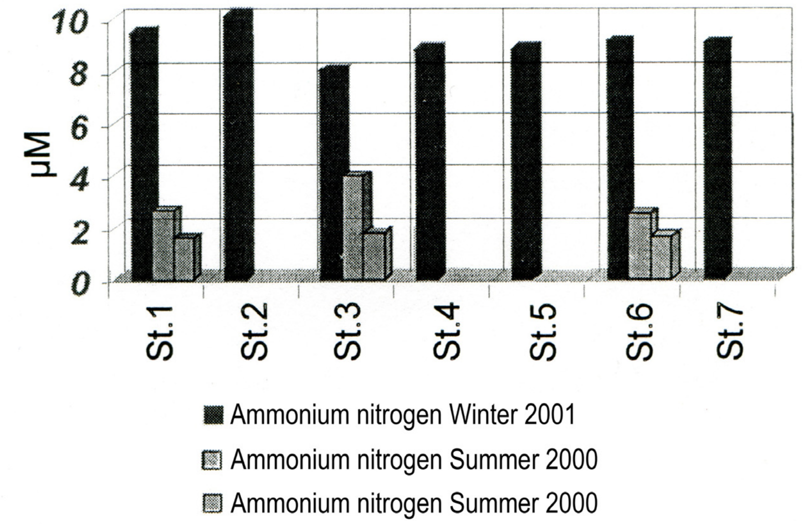


Figure 24 Distribution of dissolved phosphate(A), nitrite(B), ammonium(C), silicate (D) (all in µM) and SPM concentration(E) (in mg/L) in the surface Ob waters upstream of Salekhard in summer 2000 and winter (December) 2001 (Makkaveev et al., 2002, A).

Fig.24-d

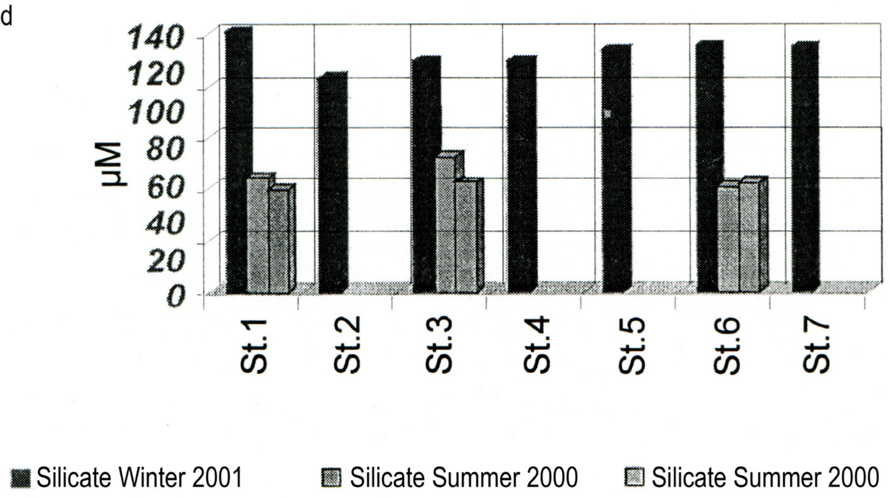


Fig.24-e

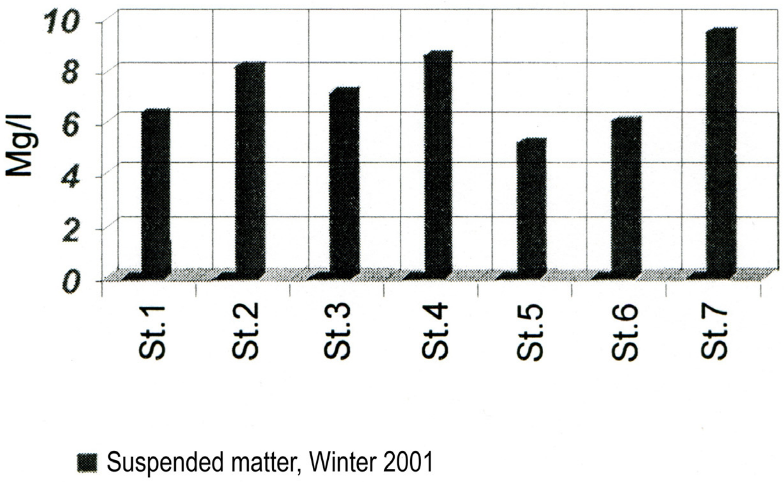


Figure 24 continued.

There are also some differences between mainstream stations and coastal stations. The coastal stations (1, 2, 6, 7) are characterized by higher concentrations of SiO_2, NO_3 and NO_4, but not of PO_4 compared to mainstream stations (3, 4, 5).

From 15 to 28 September 2002 water samples were obtained on board of the passenger ship "Mekhanic Kalashnikov" along its route Salekhard-Antipayuta-Salekhard (Fig.14). The route covered latitudes from 66°30N to 69°06N, from the lower course of the Ob River to the southern part of the Ob and Taz Estuaries. The results are shown in Table 7.

The work was done in a period of low water level. The water temperature decreased from south to north from 8° C to below 4° C. A decrease of water temperature of about 0.5-1° C was noticed on the way back (Fig. 25 A).

Dissolved O_2 content in water decreased at the entrance into the Ob Guba, and further increased mainly due to decrease of temperature (Fig.25 B).

The pH increased from the Ob River to the Ob Guba and decreased from 70^0N to north as a result of inflow of acidic water from swamps and frozen soils. That is in good agreement with data on the reinforcement of thermoabrasion of frozen soils (Semiletov et al., 1998) (Fig.25 C).

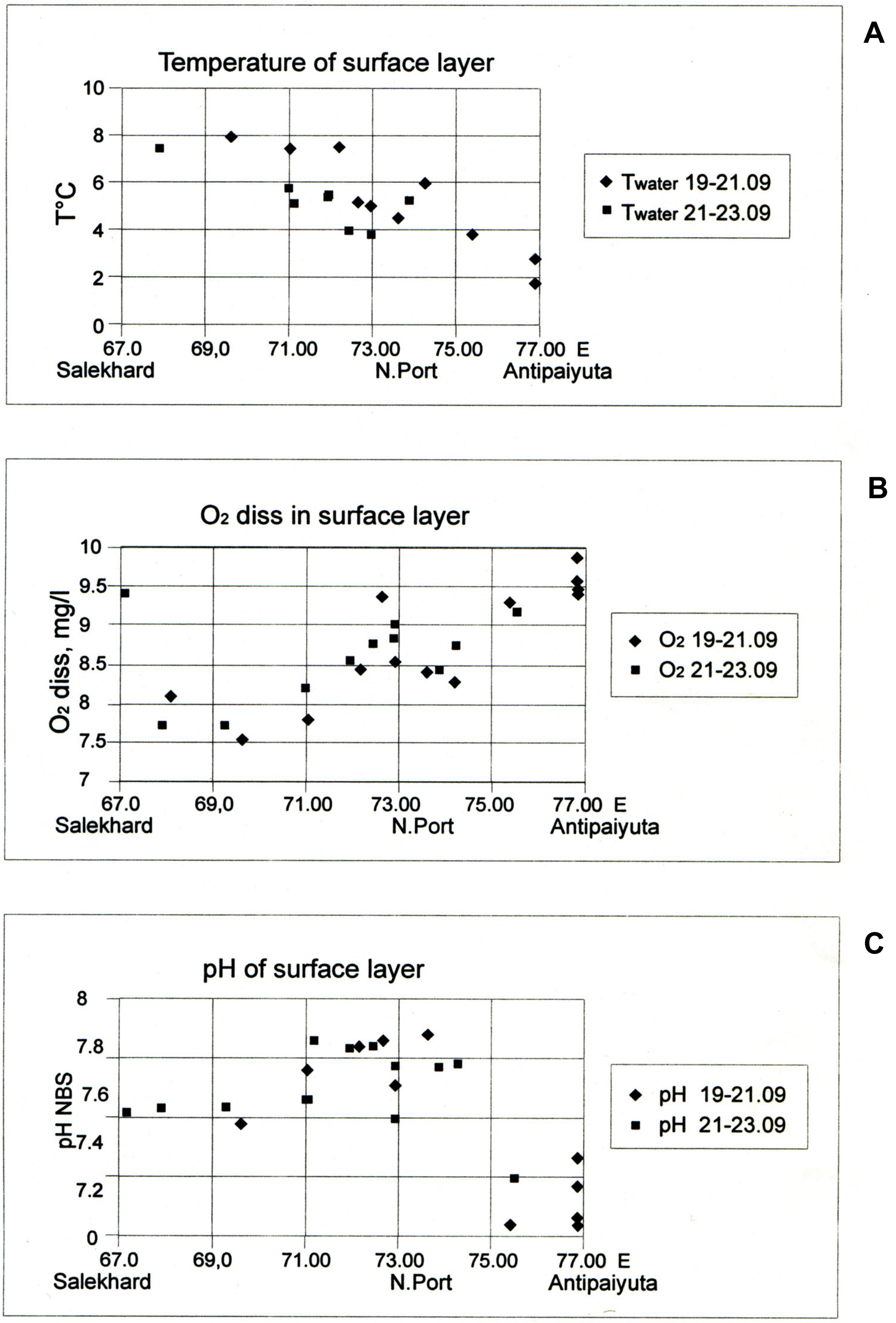


Figure 25 Distribution of temperature (A), dissolved oxygen (ml/l)(B), pH (NBS)(C), phosphate(D), silicate(E), nitrite(F), nitrate(G) and ammonium(H) (all in µM) from Salekhard to Antipayuta and back (the Taz Bay, Fig. 14) in surface waters of the Ob River and Estuary in September 2002 (Makkaveev et al., 2002, B).

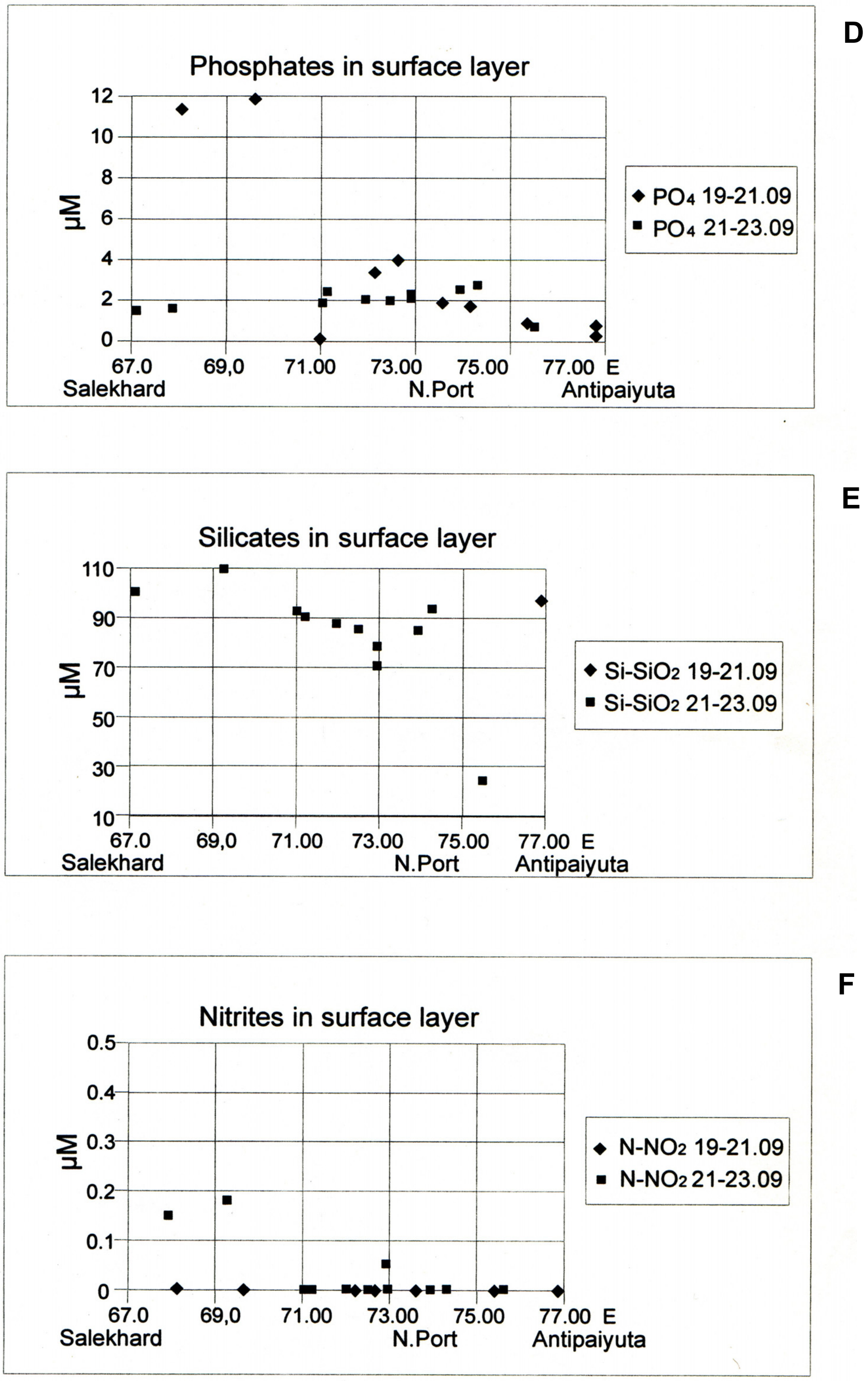


Figure 25 continued.

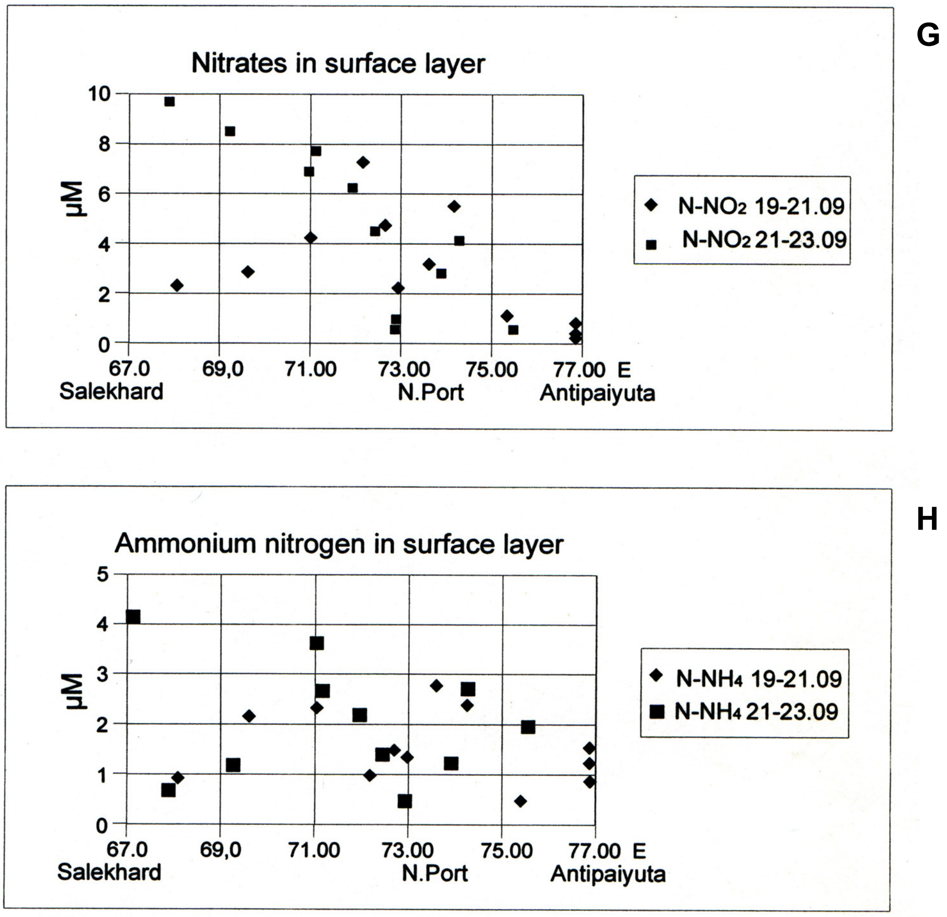


Figure 25 continued.

The NO_2 concentration was near the analytical detection limit for the majority of samples. The NO_3 concentration was higher than at summer time, but did not meet the winter maximum. Its concentration decreased on the transect from the Ob River to Taz Guba from 10 to less than 1μM and was very low near the shores at Novyi Port and Autipayuta (Fig.25 G). The NH_4 concentration was lower than in previous determinations and, like NO_3, lowest concentrations were found near Novyi Port and Antipayuta.

The concentration of PO_4 was relatively stable along the route of the ship except on two locations in the lower Ob River. The concentration of dissolved silicates decreased generally from south to north, highest concentrations were detected in the river.

The lower concentration of nutrients and higher concentrations of dissolved O_2 near the shores in the Ob Estuary may be explained by the autumn plankton bloom in water.

The obtained data are characteristic for the transition period from summer to autumn-winter. They show a significant biological activity and good ecological water conditions of the lower Ob River and the Ob and Taz Estuaries.

The seasonal variations of nutrient concentration in Ob and Yenisey are shown in Fig.26. The mean monthly concentration of NO_3 usually increases in spring, whilst lowest concentrations are found in summer. The PO_4 concentration does not show such variability. Gordeev, 2000 proposed that high NO_3 concentrations in winter are due to the input of underground waters which could introduce up to 20% inorganic nitrogen and 15% inorganic phosphorus (Gordeev et al., 1999). Dilution by melting water in spring and assimilation of nutrients by phytoplankton cause low concentrations in summer time.

Data on seasonal variations of dissolved silica are available for the Lena River only (Fig.27). During the flood time, melting ice waters decrease SiO_2 concentrations by 20-30%.

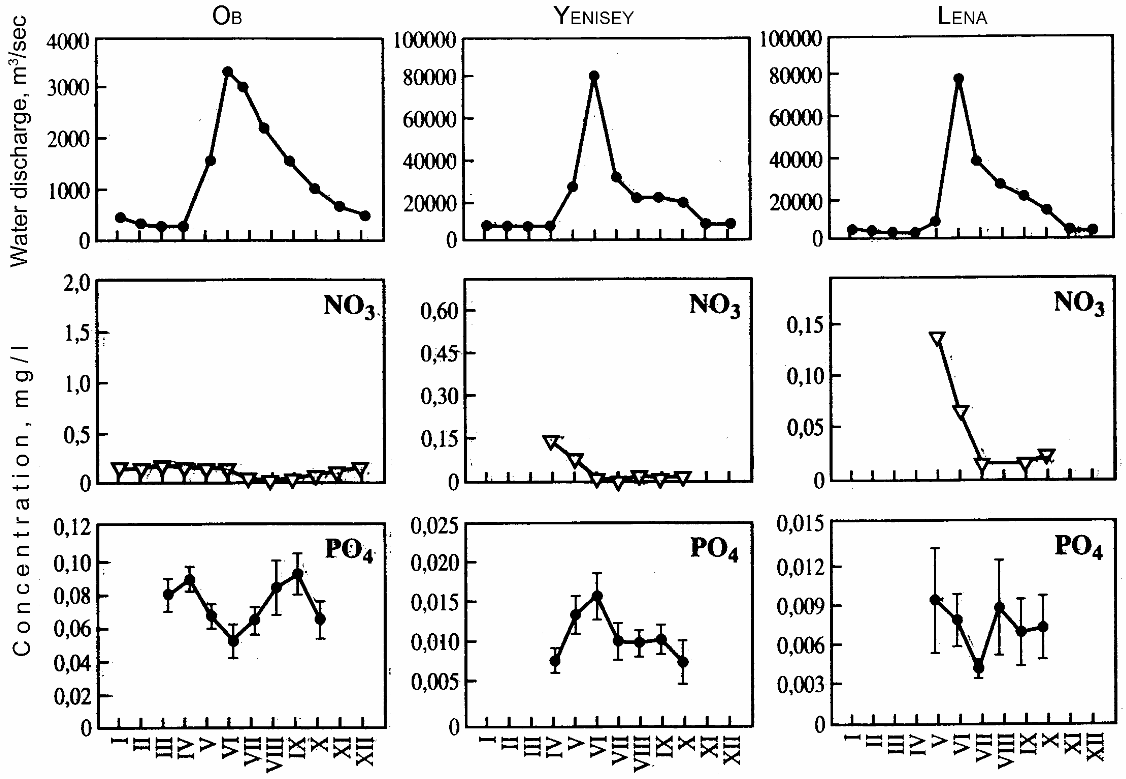


Figure 26 Seasonal variations of water discharge and dissolved nutrients in the Ob, Yenisey and Lena Rivers (Holmes et al., 2000).

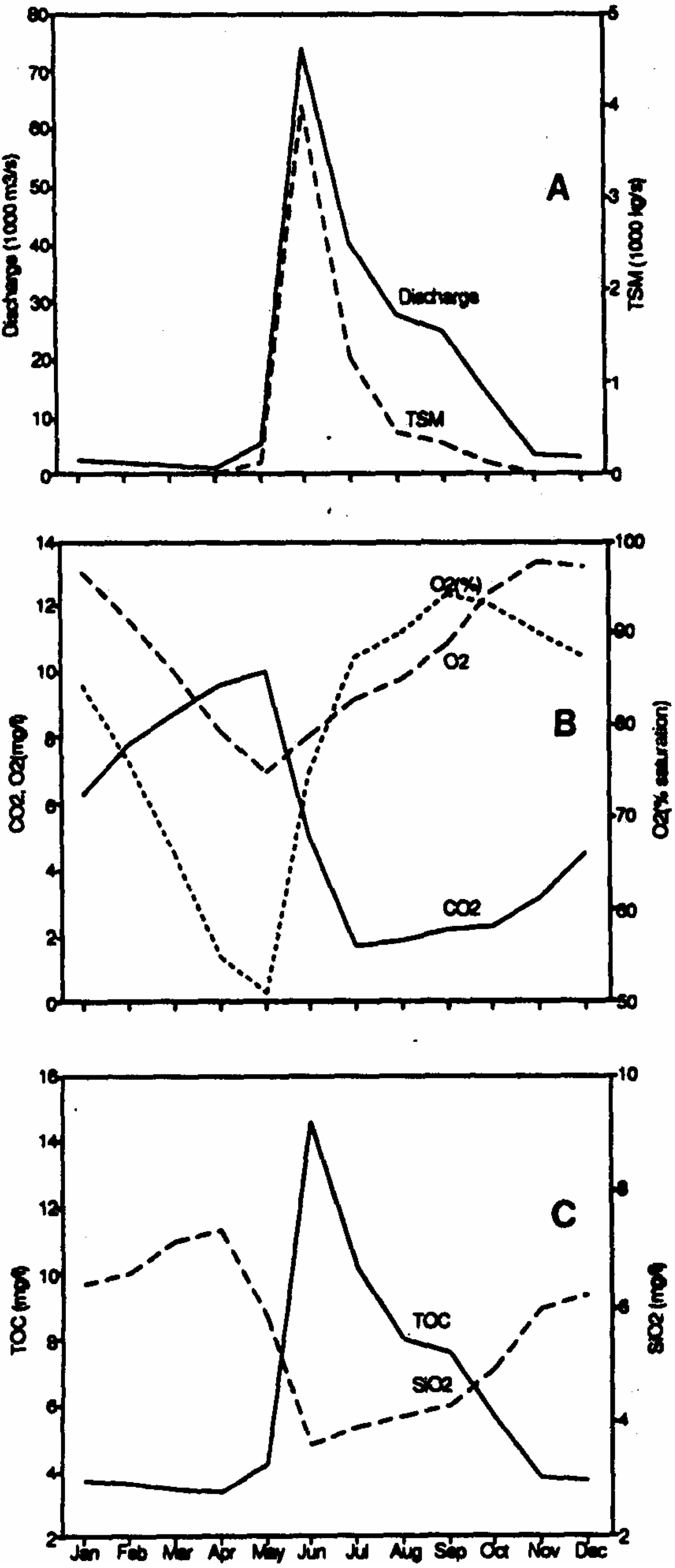


Figure 27 Seasonal variations of water discharge and SPM (A), dissolved oxygen and carbon dioxide (B), TOC and SiO_2 concentrations (C) in lower reaches of the Lena River (Cauwet and Sidorov, 1996).

4.2.1.4 Trace elements

The first reliable data on dissolved HMs in Russian Arctic rivers were obtained in the 90s of the last century in frameworks with the programs SPASIBA, Laptev Sea System and SIRRO. Generalization of these materials results in the assessments of the average concentrations of dissolved HMs in Russian Arctic rivers (Table 8). The comparison to global averages shows that no pollution of Arctic river water occurred. The concentrations of the most dangerous HMs such as Pb, Cd, Hg, As in these rivers are even lower than the global average. The comparison of the Ob and Yenisey reveals that concentration of many metals (Cu, Ni, Pb, Hg, Fe) is 1.5-3 times higher in the Ob. Only the concentration of Zn and Cd are higher in the Yenisey.

However, the HM pollution is much higher along the mainstream of the river from its upper reach to its mouth. We have a possibility to do it on the example of the Irtysh River from its head to the confluence with the Ob River. The data are taken from the works by Panin (2002) and Gordeev and Vlasova (2002). Panin with co-authors (Panin and Sibirkina, 2000; Panin, 2002) have carried out analyses of water samples from Irtysh and its tributaries in Kazakhstan between 1984 and 1996. It was shown that the combination of anthropogenic impact and specific natural geochemical anomalies (geochemical provinces with anomaly high concentrations of P, As, B, Sr (Il'in and Syso, 2001)) causes high concentrations of many dissolved heavy metals in the upper Irtysh River and its tributaries. Unfortunately, the water samples were not filtered before analyses. There is a reference to "Unified Methods of Water Analyses in the USSR" (1978) and a note on the analytical methods, which were ICP-OES and GF-AAS (for Cd determinations) (Panin, 2002).

In comparison with global averages these results show 70 times higher Zn concentrations, 15 times higher Cu concentration. The Co concentration is 19 times higher, Pb concentration is 550 times higher, Cd concentration is 72 times higher, Cr concentration is 8 times higher, Mn concentration is 4.6 times higher than global average.

In July 2001, the authors of the paper Gordeev and Vlasova (2002) have participated in expedition on board of a small vessel "Mirazh" (34t deadweight) to collect water samples along the Irtysh River in its middle course from Omsk city to the confluence with the Ob River on 18 stations (Fig 28). Samples were filtered on board immediately after collection through 47 mm nucleopore filter in plastic Millipore funnel. The trace element analyses were carried out by AAS method in flame and flameless modifications in Moscow. The results are presented in Table 9.

Interpretation of the results needs to take into account the following. The water of the middle Irtysh (down stream Omsk city) has a yellow-gray colour due to clayey-silty suspension (chemical composition of suspended matter will be considered in section 4.2.2.7). Along 1834 km from Omsk city to the confluence with the Ob River 7 samples were taken in the Irtysh tributaries, and 6 of them were with brown waters of swamp genesis (except Tara River) (Fig.28). The chemical composition of these waters is sharply differed from typical yellow-gray waters. Concentrations of Fe and Mn are very high in brown waters as well as Ni, Co and Zn (in lesser degree). Concentrations of other elements (Cu, Pb, Cd, Cr, Hg) are comparable in both types of waters. After confluence of the main stream with yellow-gray waters with waters of tributaries with brown waters the concentrations of Fe and Mn increase in 6-7 times and Ni and Zn in 1.5 time in mixing waters of the Irtysh River downstream. So, the reasons of the increase of Fe, Mn, Zn and Ni concentrations are obviously natural.

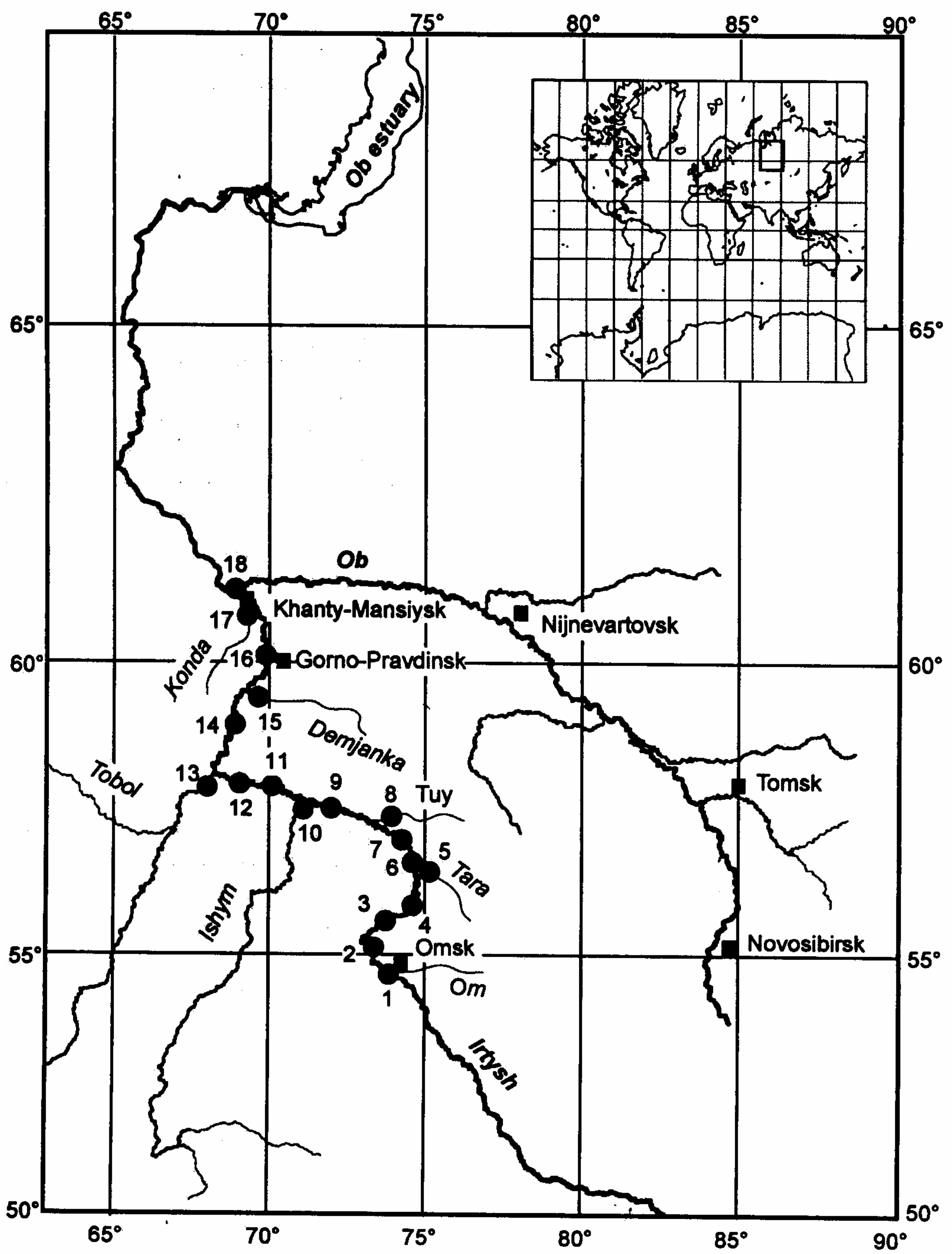


Figure 28 Sampling locations in the Irtysh River and its tributaries (July 2001).

In the lower course of the Ob and in the estuary the concentrations of all analysed metals were found to be on background level or even below (Table 8 and 9). Unfortunately, this type of work has not been carried out on the Yenisey.

The available data show a regular decrease of heavy metal concentrations (excluding the influence of brown water tributaries) from the upper Irtysh towards the Ob Estuary.

Very large water discharge and an ability of natural self-purification of the Ob-Irtysh River system are the most important reasons of this situation. Because of the few reliable measurements, these conclusions are preliminary. Also, the results of different authors appear to be badly comparable due to serious analytical problems.

To a certain extent, we have a possibility to take into account the seasonal variations of HM concentrations in the Ob River. In water samples from December 2001 the concentrations of some dissolved HMs were measured by the modern methods (Table 10). The concentrations of almost all heavy metals are significantly higher in winter time than in the summer-autumn period of the same year. Unfortunately, the amount of data for the winter time is very limited and there are no results available for period of spring flood, when the main masses of substances are transported by the river to the sea. Nevertheless the analyses were taken into account to assess the average HM concentrations in the Ob River water (Table 8).

4.2.2 Suspended particulate matter (SPM)

4.2.2.1 SPM concentration in Arctic rivers

Average multi-annual concentration of SPM in Ob and Yenisey is 37 mg/l and 8 mg/l respectively. These are very low concentrations in comparison with the global average of 530 mg/l (Gordeev, 1983).

The monthly concentration of SPM in Ob, Yenisey and Lena vary substantially from year to year (Fig.29).

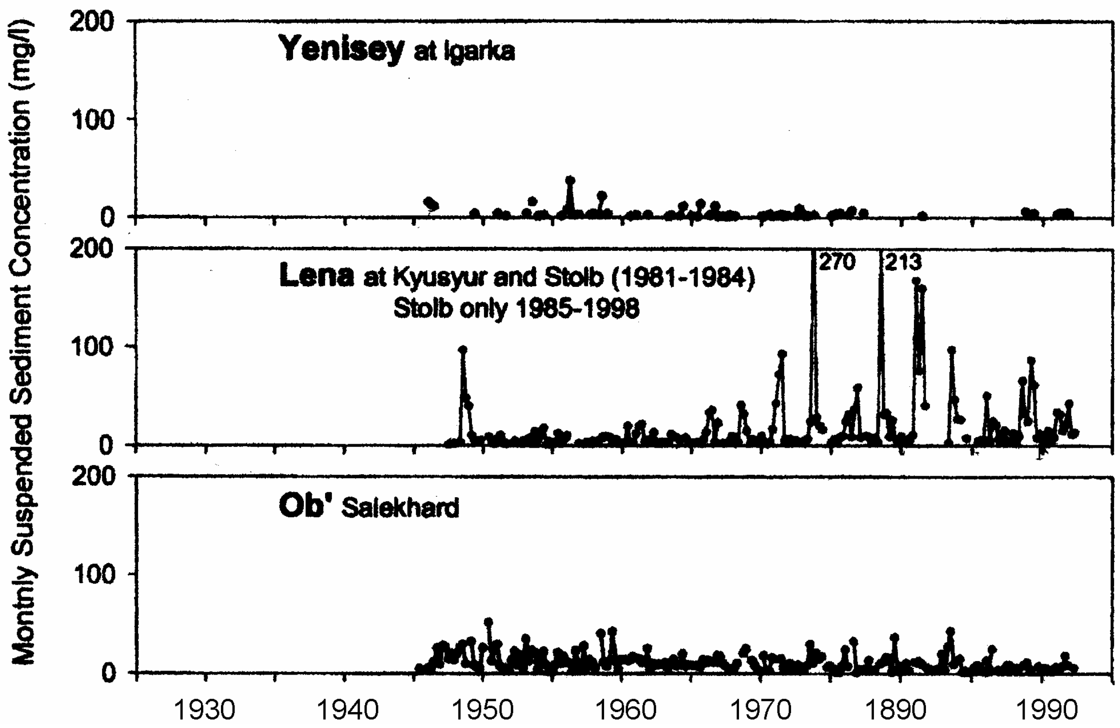


Figure 29 Monthly suspended sediment concentrations the Ob, Yenisey and Lena Rivers (Holmes et al., 2002).

4.2.2.2 Grain-size distribution in SPM

During the 49-th cruise of the R/V "Dmitry Mendeleev" to the Kara Sea and the Ob and Yenisey Estuaries (September 1993) samples of SPM were collected by separation of large volumes of water. The SPM fractions <4, >4, >8, >16, >32 and >50 μm were separated by elutriation (see Section 3.1.). Because of small weights of the samples (few tens of mg) three samples of SPM from the Ob Guba with salinity about 0 and two samples of the Yenisey Bay with salinity 0.5-1.9 ‰ were combined (Fig.7).. The grain size distribution is shown in Fig.30. The 6 fractions belong to the scale of silts. The fraction <4 μm consists of very fine silts and clay particles.

The grain size distribution of SPM from the upper Ob and Yenisey Estuaries are very similar for both estuaries. It gradually decreases from the finest particles (<4 μm) to the most coarse ones (>50 μm). It is worthy to note that a small pick in a range of size 32-50 μm was found in SPM of both estuaries..

Fig. 31 presents the grain-size distribution of SPM at station 13 (BP 2000, Fig.10) in the Yenisey Estuary (Beeskow and Rachold, 2003). A small peak in the range from 30-50 μm grain size was found in SPM in pycnocline water.

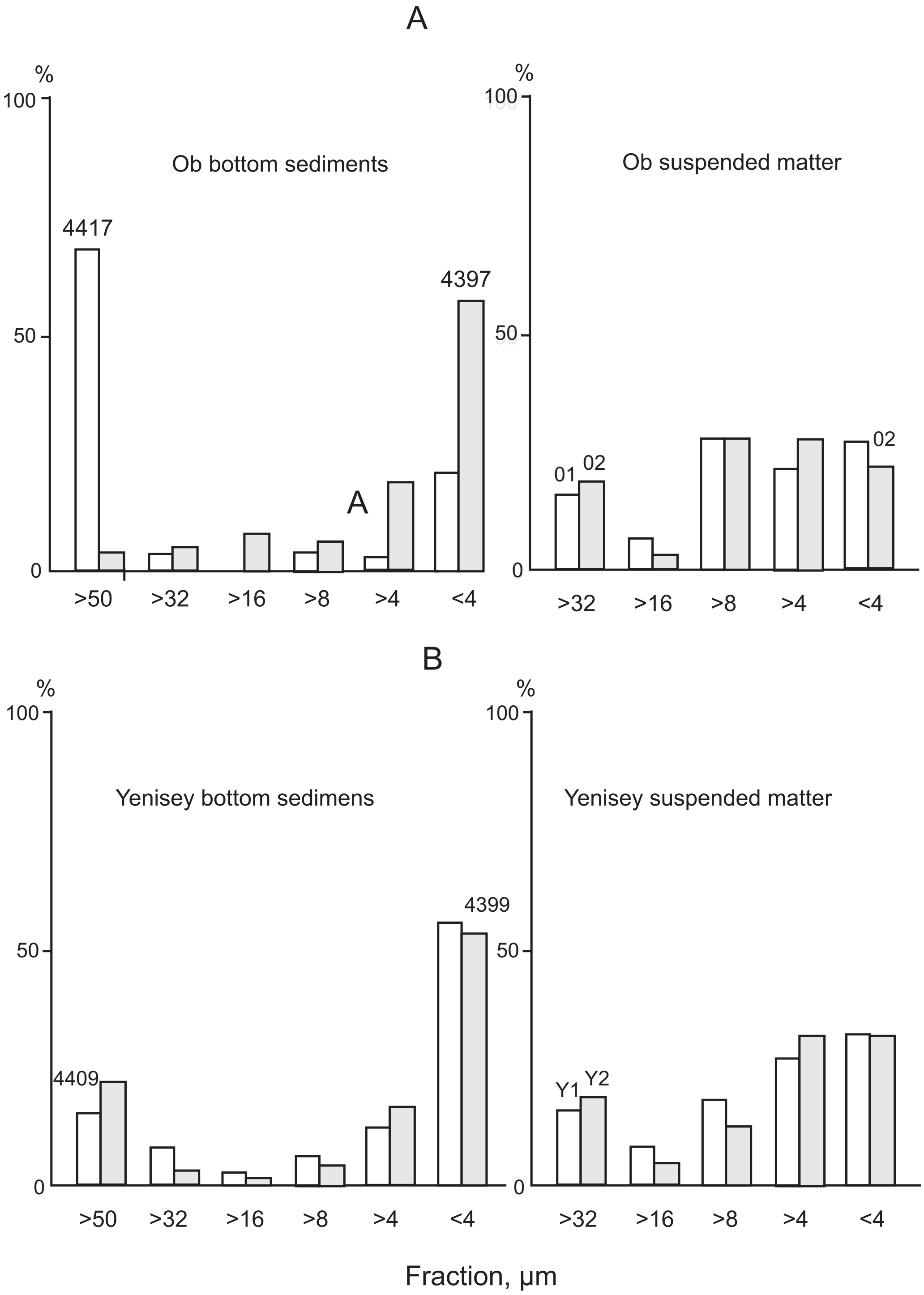


Figure 30 **Grain-size spectrums of surface suspended matter and bottom sediments in the Ob (A) and Yenisey (B) Rivers and Estuaries.**

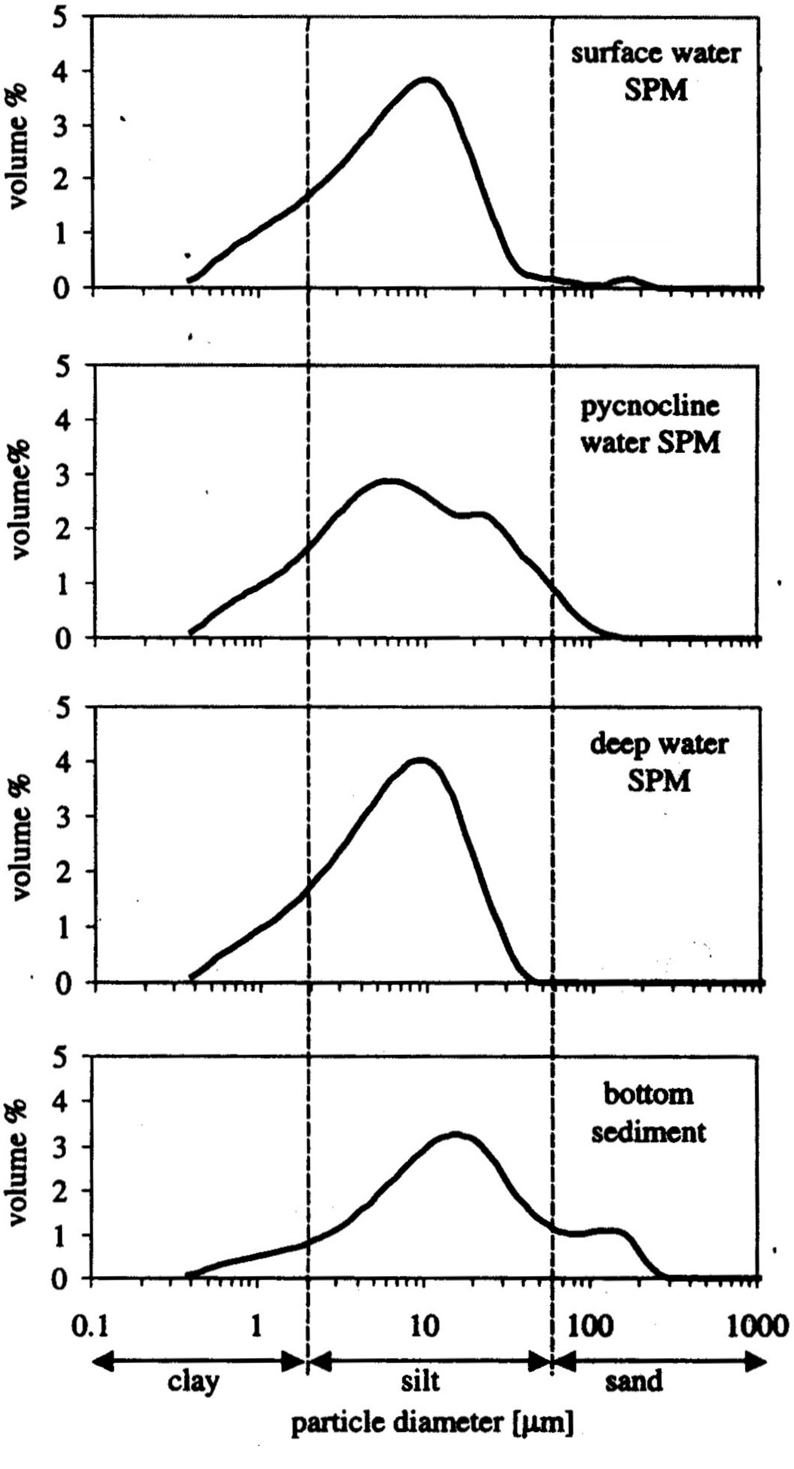


Figure 31 Grain-size distribution of SPM and bottom sediments at station 13 (Yenisey Estuary, BP-2000) (Beeskow and Rachold, 2003).

4.2.2.3 Mineralogy

SPM of Ob and Yenisey consists of quartz and Al-Si minerals (Lukashin et al., 1999). Among the clay minerals in SPM and in surface bottom sediment smectite prevails (Shelekhova et a., 1995; Levitan et al., 1996; Gorbunova, 1997; Muller, 1998; Washner et al., 1998; Muller and Stein, 1999) (Table 11). The main source of this mineral is the plateau-basalt and tuff of the Putorana Mountain in West Siberia.

The clay mineral content in SPM of Ob and Yenisey is very similar, as well as in the bottom sediments of both estuaries.

4.2.2.4 Electron probe X-ray micro-analysis (EPXMA) of SPM

Electron probe X-ray micro-analysis can be used to examine the morphology and chemical composition of individual particles in aquatic ecosystems and can thus give information about their origin and formation (Jambers et al., 1997; Lukashin et al., 1999).

The study of Yenisey SPM at salinities below 1 ‰ has shown a predominance of alumino-silicate particles which are often enriched in Fe and Ti (Jambers et al., 1997). Comparison of two SPM samples collected at the same location within 4 days show a strong variation in particle type and its abundance. Al-Si particles, Si-rich, Ti-rich and miscellaneous particle types are the main groups in SPM.

Fe-rich alumino-silicates and Fe-rich particles were found in all samples. They are especially abundant in SPM of superficial fresh water. With depth and increasing salinity their quantity decreases. The Ti-rich particles were detected in all samples. The authors were surprising to find such high abundance of Ti-rich particle type. They couldn’t explain this find (Jambers et al., 1997). Ti-rich particles may originate from anthropogenic sources like asphalt production spray, coal and other. In small quantities Mn-rich and Ca-S-rich particles were detected.

Lukashin et al. (1999) reported that Ti-alumino-silicate particles were found in all samples of SPM in the upper Yenisey Estuary. It was also observed, that particles contain high Ca and P together with Al-Si.

During EDAX analysis Au-containing particles were found in the Yenisey Estuary. Their size did not exceed 10 µm and the gold was coexisting in association with other chemical elements.

In SPM samples obtained during the 49-th cruise of the R/V "Dmitry Mendeleev" a predominance of Al-Si particles (52-88 % of total) has been observed. At least 50% of the particles were Fe-rich alumino-silicates and Fe-containing alumino-silicates. These particles also contained variable amounts of K and Ca. There are differences in the results of SPM samples obtained by filtration or centrifugation. Only the dominant particle component in the filtered samples was detected in the centrifuged samples. The absence of Ti-rich particles in the centrifuged samples can be explained by their small diameter. These very small particles might not be captured at sampling by the centrifuge method.

The filtered SPM from the Ob Estuary was studied in the work of Lukashin et al. (1999). As in the Yenisey Estuary, the Fe-Al-Si particles were prevailed. Au-containing particles in the SPM were found in combination with Cu while concentrations of Si, Al, and Fe in these particles were insignificant.

4.2.2.5 Particulate and total organic carbon (POC and TOC)

Data on POC in Ob and Yenisey Rivers and Estuaries are sparse. Most of the available data, especially these from the period of the former Soviet Union, relates to TOC, i.e. the sum of dissolved and particulate carbon. Therefore, this section considers the available materials, on POC and TOC together (Table 12). The first separate determinations of DOC and POC in the lower course of the Ob were obtained in summer 1959 by Nesterova (1960). She found in average 0.9 mg/l POC and 2% POC in SPM, the TOC was about 10 mg/l.

Multi-annual data on TOC (few tens of thousand of indirect determinations performed on unfiltered water samples by permanganate oxidation in acidic media with a correction factor of recalculation into TOC values) for the period from 1936 to 1980 have given a average value 7.1 mg/l TOC in the Ob River (Smirnov et al., 1988). The results of two small expeditions to the lower Ob River are given in Tables 13 and 14.

Similar data were obtained for the Yenisey with 7.4 mg/l TOC (Maltseva et al., 1987). The most recent data of Lobbes et al. (2000) show in the upper Ob Estuary in early autumn of 1997-1999 average fresh water POC concentration of 0.3 mg/l, and TOC of 8.8 mg/l.

There are more recent data for the Lena River (Cauwet and Sidorov, 1996) where TOC is 7.7 mg/l, similar to Ob and Yenisey. This value is lower the global average (Table 12).

POC data from December 2001 in the Ob River are especially interesting because no data are available for the period of winter low water. The SPM concentration in December 2001 was in a range from 5 to 9.4 mg/l, and only in one deep water sample (8 m depth at station 1) the concentration is very high with 22 mg/l. POC content in dry SPM varied in a range from 5.1 % to 21.9 % and is in average 12.8 %. POC concentrations were high also- 0.70 - 1.35 mg/l, in average 0.96 mg/l. Taking into account that in December water and sediment discharge are close to minimum, the results obtained have to be taken into account during the assessment of annual fluxes of POC and TOC to the ocean.

Samples of 19 stations from September 2002 (Section 3.1.8) were analyzed for their SPM concentration which was very low between 1.4 and 18.7 mg/l(Table 14). The POC concentrations (0.07-0.71 mg/l, in average 0.27 mg/l) were lower than in December 2001 although the methods of sampling and analyses were identical in both expeditions. The content of organic carbon in dry SPM was between 2.1 and 6.8 % with an average of 4.2 % and hence, was also lower than in samples of autumn 2002. SPM in the Taz Estuary appeared to be enriched in POC with values between 5.3 and 14.7 %.

The data obtained reveal significant seasonal variations of POC in Ob River and Estuary. More all year round observations on DOC, POC and TOC are needed for the Arctic rivers.

4.2.2.6 Nutrients

Data on particulate forms of nutrients are very scarce. Particulate phosphorus (PPh) was measured in the expeditions BP-1997, BP-2000 and BP-2001, and also in the expeditions to the Ob River (Salekhard) in December 2001 and to the Ob-Pur-Taz Guba in September 2002 (Table 15).

PPh content is in a range of 0.28 to 0.72%, av. 0.41% in the Ob and 0.17-0.50%, av. 0.30% in the Yenisey River. Its concentration accordingly is 0.01-0.09 mg/l, av. 0.04 mg/l in the Ob and 0.003-0.021 mg/l, av. 0.011 mg/l in the Yenisey. Particulate nitrogen (PN) content is in a range 0.28-1.59%, av. 0.9% in the Ob River and 0.78-3.07%, av. 1.32% in the Yenisey River (Table 15). We see that the Yenisey SPM is enriched by nitrogen in comparison to the Ob SPM. PN concentrations were higher in the Ob River due to its higher SPM concentration (0.035-0.14 mg/l, av. 0.09 mg/l in the Ob and 0.04-0.07 mg/l, av. 0.05 mg/l in the Yenisey). These are the total particulate forms of N and P. The organic particulate forms of the nutrient elements were assessed using Meybeck's estimates. He has used the typical river SPM ratios POC/PON=8.5 and POC/POP=22 to estimate the concentration and flux of particulate organic forms of N and P. The global values of Meybeck calculations (Meybeck, 1982) are equal for PON=0.56 mg/l, or 0.12 % on dry weight of SPM, for POP=0.21 mg/l, or 0.045 %, TON data are absent, TOP=0.53 mg/l, or 0.115 %. If these ratios are applied for the Ob River we obtain: PON=0.1 mg/l, or 0.23% (based on data of Nesterova, 1960), or 0.03 mg/l and 0.44% (based on data from September 2002). For December 2001 PON is very low with 0.006 mg/l and 0.1%. For the Yenisey the calculation of data from Lobbes et al. (2000) shows that PON equals 0.035 mg/l. Accordingly, POP estimates are as follows:

Ob:	0.04 mg/l and 0.09 % (Nesterova, 1960);
	0.043 mg/l and 0.58 % (December 2001);
	0.012 mg/l and 0.19 % (September 2002).
Yenisey:	0.014 mg/l (Lobbes et al., 2000).

Very simple calculations give the following results: POP=0.16% in the Ob and 0.12% in the Yenisey.

These are estimates only and direct determinations of organic forms of N and P is still required. A comparison with the global averages shows that PON and POP concentration in SPM of both Siberian rivers are much lower than global estimates, although their relative contents in SPM are of the same level, or even higher.

4.2.2.7 Major and trace elements

Major elements

Available data on major element composition in Ob, Yenisey and Lena (for comparison) SPM are presented in Table 16. The SPM of the Ob shows a higher content of Fe, Ti, Mn and P. In the Yenisey SPM, Mn and P concentrations are high but all other major elements are lower compared to the global average. The SPM of Ob obtained during

"BP-2001" and in December 2001 is marked by an extremely high content of Fe. 30-31 % was measured in SPM of the Polyi River, the eastern tributary of the Ob, near Salekhard in December 2001. That is 6 times higher than global Fe in river SPM. At the same time, dissolved Fe in the Polyi River was slightly below than in the Ob River (560-680 µg/l against 740 µg/l), whilst dissolved Mn in Polyi was with 855-873 µg/l, 10 times higher values than in the Ob River.

The SPM of the Polyi River is unexpectedly low in Al content with 1.1 %, and also Mg, K and Na (Si was not determined). If to assume that all Al in the Polyi SPM was in crystalline form, than the part of Fe in amorphous form would be 93.5 % of total Fe in SPM. POC is very low content with about 1 %, whereas particulate phosphorus was twice of POC. In SPM of the Irtysh tributaries with brown water of the swamp genesis 10.9 % were Fe and 0.85 % P, but the POC content was much higher than in the Polyi River (up to 9.8 %). Therefore, we suggest that the unusual high concentration of Fe and P in SPM of the Polyi and the lower course of the Ob in December 2001 was the result of underground input of the swamp water. However, this does not explain the very low content of POC.

In Table 16 new assessments of average contents of major elements in SPM of the Ob and Yenisey and in the river discharge of all Eurasian Arctic are presented. We took into account that in SPM of the Ob River in December 2001 the chemical composition was significantly distinguished from summer-autumn period. It was assumed in the calculations that between November and April SPM of the Ob had a chemical composition close to that of December. For the rest of the year the SPM composition was characterized by its summer regime. Unfortunately the winter data for the Yenisey SPM are absent.

Trace elements (except REE)

A review of recent data on trace element concentrations in SPM of Arctic rivers, including Ob and Yenisey, was published by Gordeev (2002). These data, together with recently published data by Beeskow and Rachold (2003) and Savenko et al, (2001) as well as unpublished materials of the BP-2001 and small expeditions to the low course of the Ob River in December 2001 and September 2002 are presented in Table 17.

The results for December 2001 show that, similar to some major elements and components (Fe, Ca, Ti, POC, P), the trace element content of Zn, Cu, Cd, Pb, and As is 1.4-4.0 times higher than average whilst Cr, Sr, V, Zr are equally to average content in the Ob SPM. Previously, we suggested that higher water mineralization and higher content of amorphous Fe and POC in SPM is caused by underground water, the main source of water in winter. These very effective sorbents can concentrate heavy metals such as Zn, Cu, Cd, Pb, and As. The high heavy metal content in the Ob SPM in December 2001 is probably connected with these natural processes.

A comparison of average concentrations of trace elements in Ob and Yenisey SPM samples shows that SPM of the Ob River contains slightly more Zn, Pb, V, Zr, As and less Cu, Cd, Cr, Sr than SPM of the Yenisey River. Compared to global average the contents are very close or even slightly below global magnitudes. Only As is 2.5 times higher in the Yenisey and 7.2 times in the Ob River. As shown in the next chapter, this enrichment has a natural character.

In Table 17 we present our new evaluations of average contents of trace elements not only in SPM of the Ob and Yenisey Rivers but also in general for SPM of Eurasian Arctic rivers. For the calculations, SPM data of the three largest rivers Ob, Yenisey and Lena, as well as that of Yana and Khatanga (Rachold, 1999) have been used. For all other rivers the concentration of trace elements in SPM is assumed to be equal to average concentrations in SPM of the Ob, Yenisey and Lena.

Rare-Earth Elements (REE)

Gordeev et al. (1995) analyzed REE in centrifuged samples of the Yenisey and the Ob Rivers (Table 18). REE concentrations in SPM of the Yenisey River were measured by Beeskow and Rachold (2003). Latter data are very close to average composition of the upper continental crust, whereas the data of prior authors are noticeably lower. This is probably due to differences in sampling methods where during the centrifugation of water a part of the finest sediment can get lost. The REE distribution of the Yenisey SPM is very similar to that of the North American shale Composition (NASC), as seen from its flat NASC-normalized REE pattern (Fig.32 A and B). The REE patterns of the Lena and Khatanga are shown for comparison. Lena SPM is characterized by an enrichment in light REE (LREE) relative to heavy REE (HREE), which is typical for river-borne SPM (Goldshtein and Jacobs, 1988) whilst Khatanga shows with its overall depletion of REE's and a positive Eu-anomaly the pronounced influence of the Siberian Trap Basalts in its catchment (Beeskow and Rachold, 2003). The REE patters of Yenisey and Ob SPM (centrifuged samples, INAA determinations) show similar to the Yenisey SPM (filtered samples, ICP-MS determinations) character (Fig.32 C and D) but the ratios C/C^{NASC} are lower because the lower REE contents were measured in centrifuged samples (Table 18).

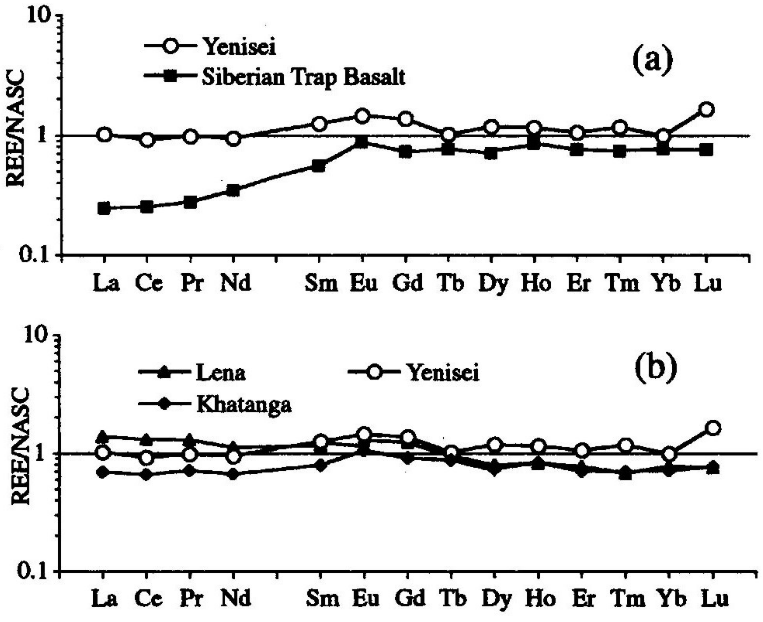


Figure 32 NASC - normalized REE patterns of Yenisey SPM and Siberian Trap Basalts (A) and REE pattern of Lena and Khatanga SPM compared with Yenisey SPM (B) (Beeskow and Rachold, 2003); REE patterns of Ob SPM and Yenisey SPM (1993) (C- river end member, D- marine end member) (Gordeev et al., 1995).

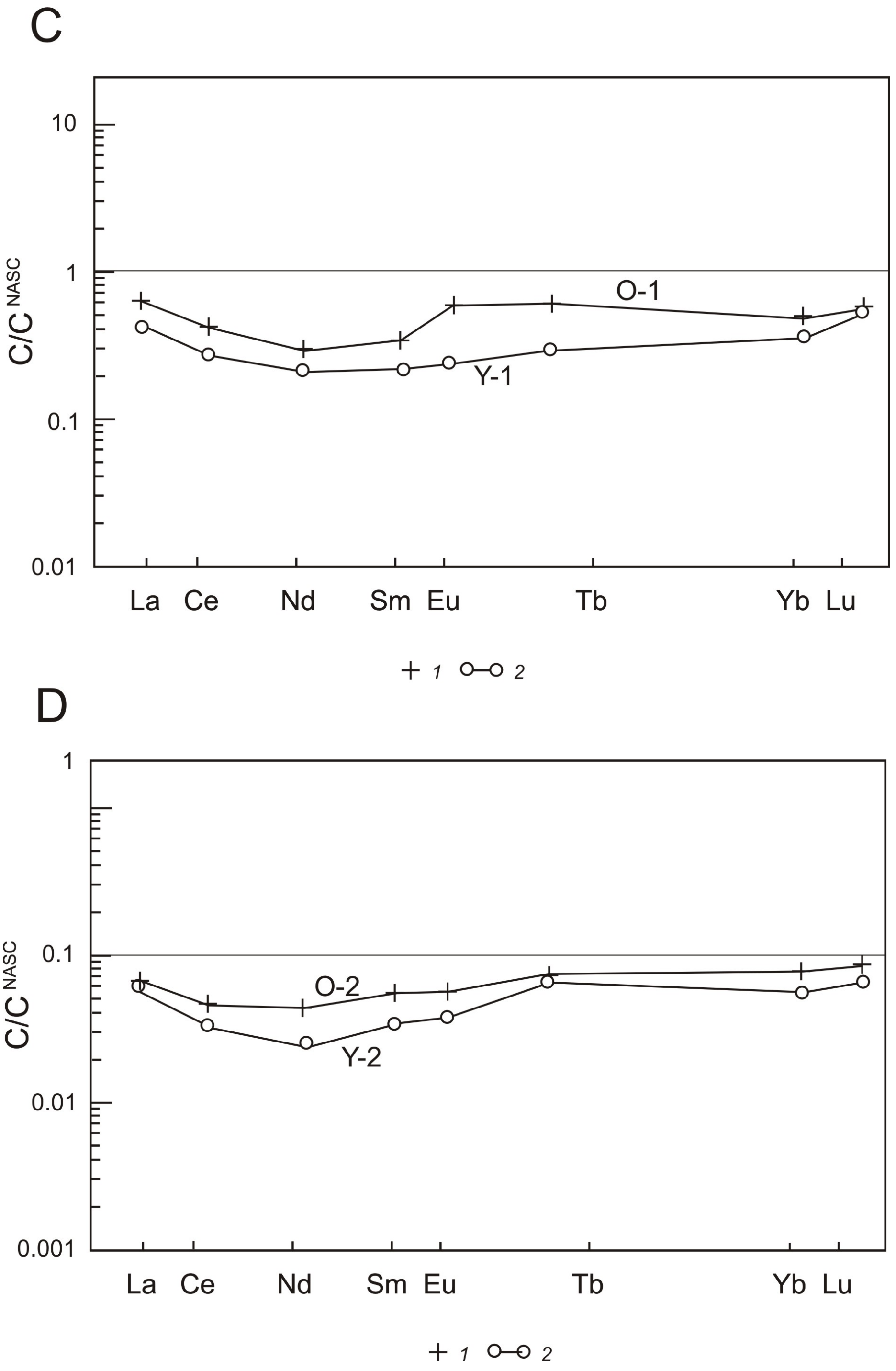


Figure 32 continued.

Grain-size distribution of chemical elements in SPM

As shown in Section 4.2.2.2 the amount of SPM from the two rivers gradually decrease from the finest particles (< 4µm) to the most coarse (>50µm) with a small peak in a range of 32-50 µm. INAA determinations of some major and trace elements in small samples of different size SPM fractions show that there are three distinctive groups of elements (REE will be discussed below):

1) Ca, Cr, Hf, Th – concentrated in the coarser fraction;

2) Na, Co, Rb, Sc – monotonous distribution;
3) Fe, Cs – concentrated in the finer fraction.

Note several elements such as Si, Al, K, Mg, Cu, Pb, Ni, Zn, which are normally concentrated in finer fractions were not determined in these SPM fractions.

Ca is abundant in fraction >50µm. The clay minerals, kaolinite, chlorite and illite particularly, do not contain much Ca. Carbonate fragments of shells may play an important role in Ca distribution in SPM.

Trace elements like Hf and Cr are normally concentrated in grains of ore and accessory minerals that may form associations with unstable organo-mineral aggregates. It was also shown, that coarse quartz particles are covered by Fe-Mn hydroxides (Gibbs, 1977; Schoer and Eggersgluess, 1982). This occurrence may lead to a more uniform distribution of trace elements in the grain-size fractions of SPM. The distribution of Fe and Hf as the elements of two different groups (Fe in group 3 and Hf in group 1) is shown in Fig.33. One can observe that the element distribution in the grain-size spectrum of SPM of two rivers is very similar and that it is quite uniform compared to bottom sediments (see Section 4.4.7.2).

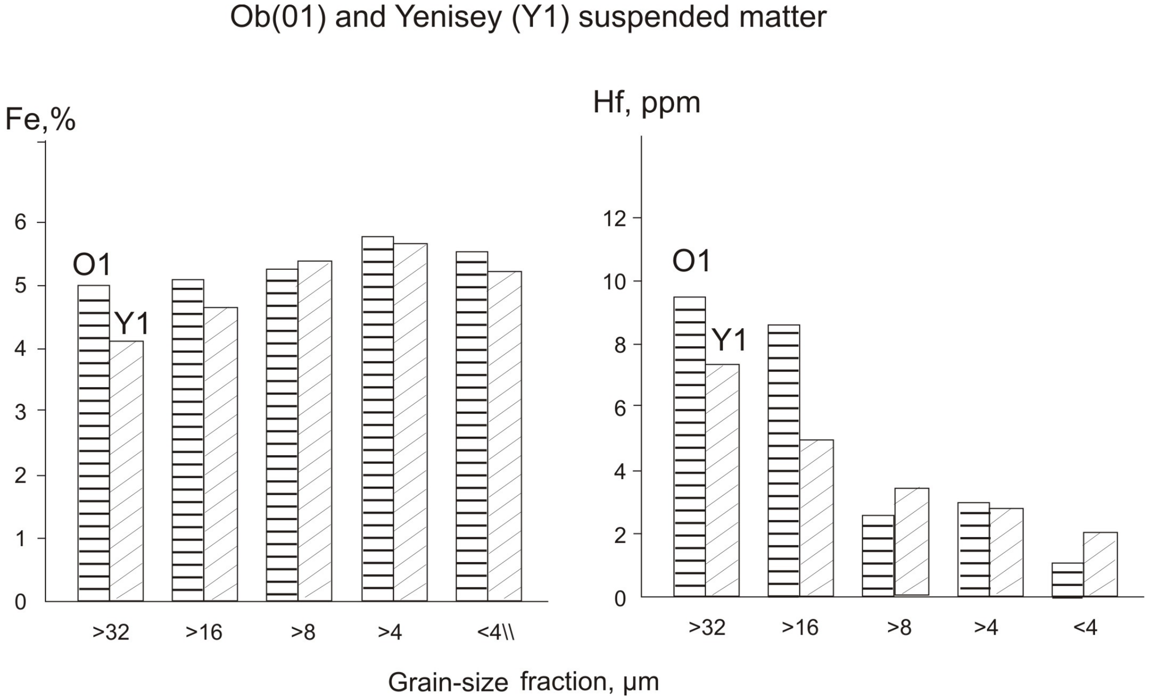


Figure 33 Fe and Hf in grain-size fractions of Ob and Yenisey SPM.

Little is known about the REE river input to the oceans. It was shown that the main of REE occur in river mainly in colloidal and particulate form whereby HREE predominantly concentrate in fine suspension and LREE in coarse fractions (Hoyle et. al., 1984; Goldshtein and Jacobsen, 1988; Elderfield et. al., 1990). The coefficient of contrast (ratio of element concentration in coarse fraction to its concentration in fine fraction) in size fractions of SPM is shown in Fig.34. The use of this coefficient is a simplification because fractional changes of REE are not always uniform. The picture shows that practically all REE in SPM of both rivers (O1 and Y1) are concentrated in the coarse fraction (except Eu and Tb in Y1). Shown (Balashov, 1976; Gurvich et. al., 1980) that in course of weathering the REE fractionation occurs, the main result of which was a relative enrichment of coarse fraction by LREE. A sorption complex, enriched middle and heavy REE, was taking out predominantly in dissolved form. Consequently, we find LREE enrichment in coarse particles. Clay minerals and flocculated Fe in fine fractions are very good sorbents of REE. We suggest that a sorption complex is responsible for Eu, Gd and Tb concentrations in fine suspension of the Yenisey and for low coefficient of contrast of these lanthanides in the Ob SPM.

The iron hydroxide film on quartz and other particles may enrich HREE in coarse fractions of SPM (Hoyle et. al., 1984). HREE enrichment of coarse suspension may be explained by an analogy with Hf case, i.e. by capture of ore and accessory minerals grains with HREE by organo-mineral aggregates.

The average shale normalized REE patterns of SPM in Ob and Yenisey in different grain-size fractions are shown in Fig.35. We do not find any significant difference between the REE patterns for grain-size fractions in both rivers. In the Ob SPM (sample O1) a positive Eu-anomaly is present in different fractions; in the Yenisey SPM (sample Y1) this anomaly is evident for the grain size fraction >16µm only. A distinction of REE concentration in fine and coarse fractions is of quantitative character only, the REE patterns are similar for both rivers.

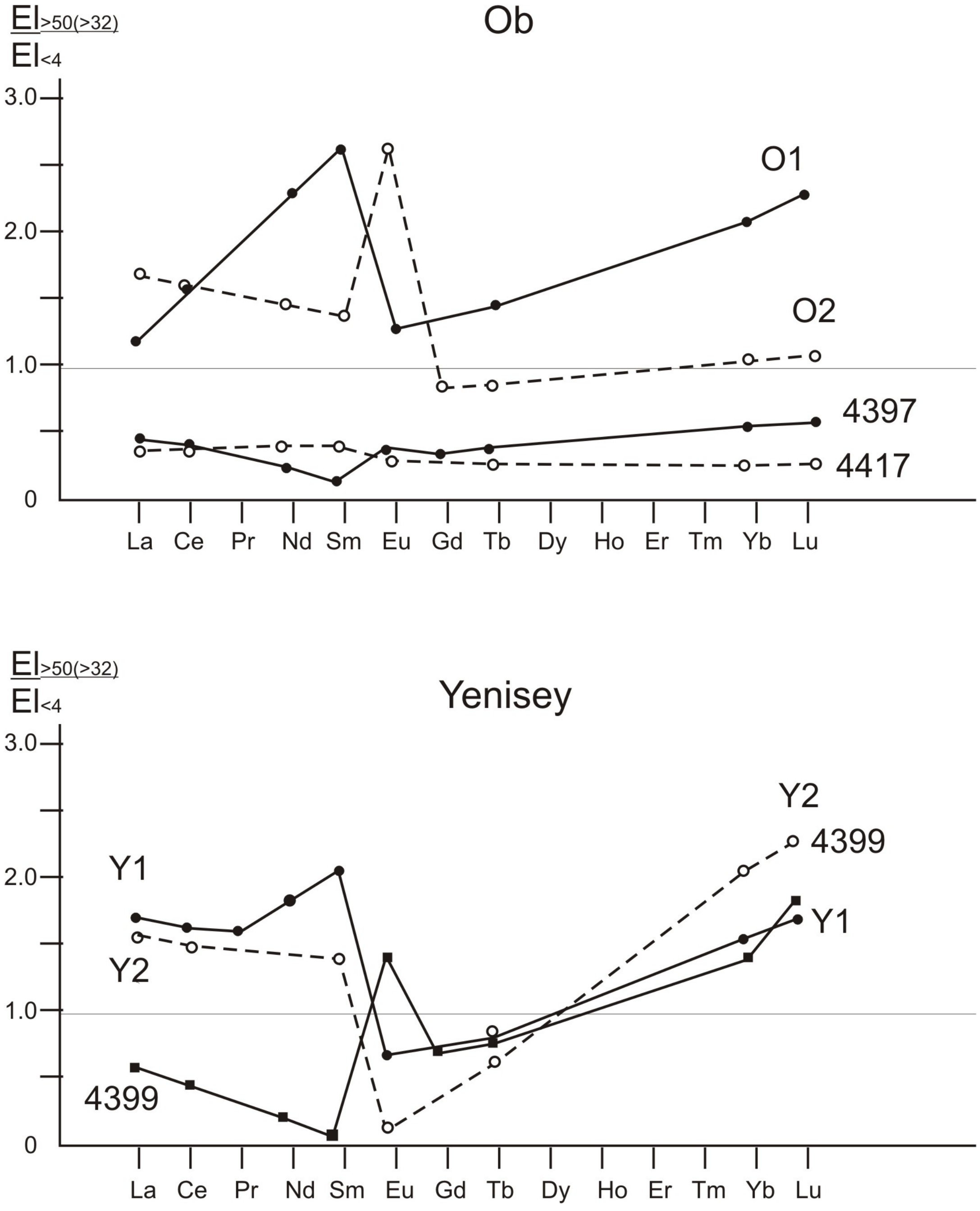


Figure 34 **Coefficient of contrast (ratio of REE concentration in coarse fraction to its concentration in fine fraction) in SPM (Ob- O1 and O2; Yenisey- Y1 and Y2) and bottom sediments (Ob- Sts. 4397 and 4417, Yenisey- St. 4399).**

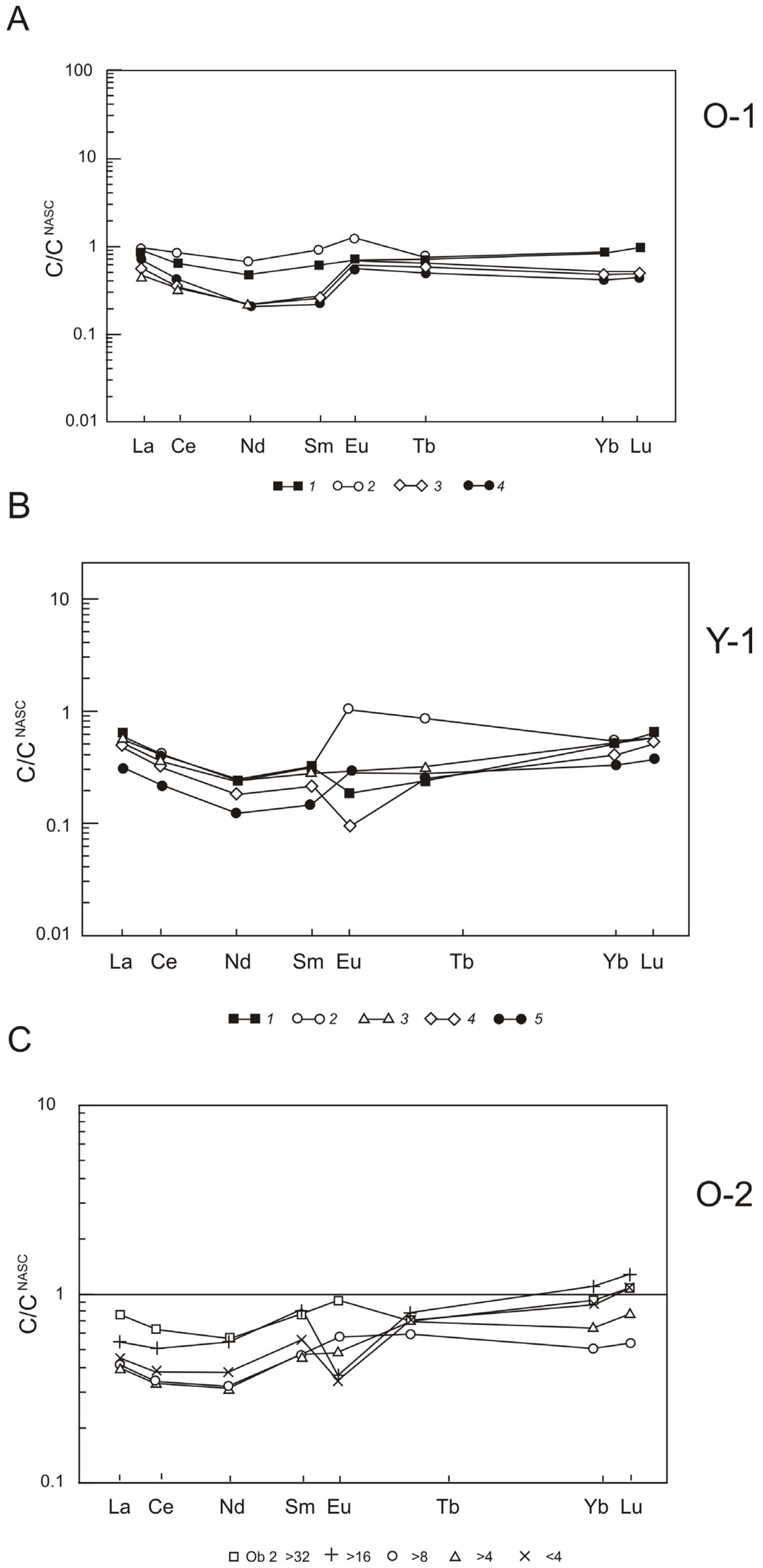


Figure 35 Shale normalized REE patterns in different grain-size fractions of SPM (A- Ob River end member O1, B- Yenisey River end member Y1, C- Ob marine end member O2, D- Yenisey marine end member Y2), 1 >32µm, 2 >16µm, 3 >8µm, 4 >4µm, 5 <4µm.

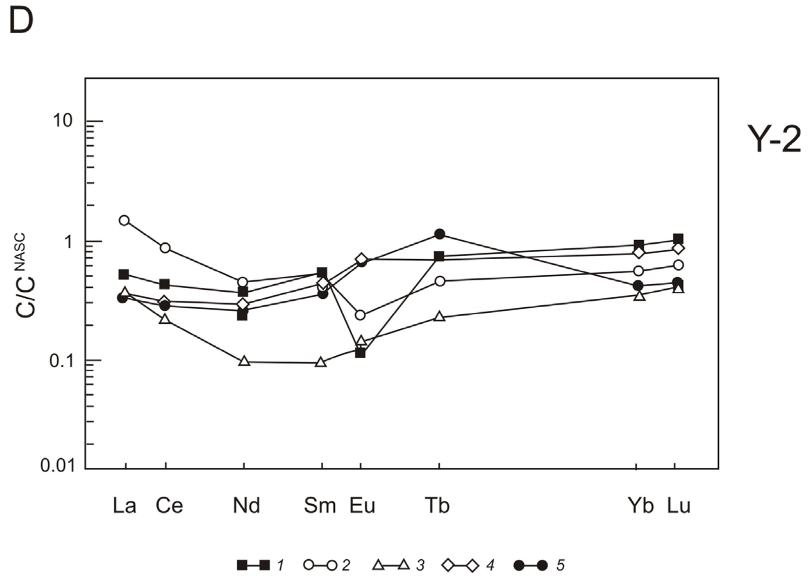


Figure 35 continued.

Chemical composition of the Irtysh SPM

Major and trace elements, POC and P_2O_5 determination was carried out for 19 SPM samples of Irtysh and its tributaries (Table 19, Fig. 28). On the first stations below Omsk the water has yellow-gray colour due to its high Al-Si concentration in SPM. The first two tributaries Tuy and Ishim carry brown water, which originate from swamps. The input, however, is too small to change the overall colour of the Irtysh water. After confluence of the Tobol River the Irtysh becomes dominantly brown until its confluence with the Ob River.

The variations of SPM concentration and its content of Al_2O_3, Fe_2O_3, CaO and POC along the mainstream of the Irtysh River from Omsk down to the confluence the Ob River (below c. Khanty-Mansiysk) are shown in Fig.36. The SPM concentration of the Irtysh River ranges from 10 to 29 mg/l, the highest SPM concentration, with an average 38.9 mg/l, was detected in the Tara River. Generally, the brown coloured tributaries are characterized by low pH (6.5-7.1) and SPM content (8-17 m/l). The Al_2O_3 content of the Irtysh SPM is constant up to the Tobol River (12-14 %) and decreases to 8.17 % at the confluence with the Ob River. The Fe_2O_3 concentration remains constant up to the Tara River inflow (5.0-5.5 %), afterwards it increases to 15 %. Similarly, the CaO concentration increases constantly from 1.3-1.5 % to 2 % after the Tara inflow. The POC concentration varies in a range of 0.7 to 1.0 mg/l (exclusive station 1) and increase up to 1.3 mg/l after the inflow of the Tobol River. The behaviour of P is similar to that of POC. Variations of K_2O, MgO, Na_2O and TiO_2 along the river are almost identical to that of Al_2O_3, their concentrations remain stable in the middle river and decrease significantly in the lower river. The trace element concentration is relatively stable, especially that of Cu, Ni, Co, Cr, and V. Variations of Zr and Sr concentrations along the river are similar to that of Al_2O_3 and CaO respectively.

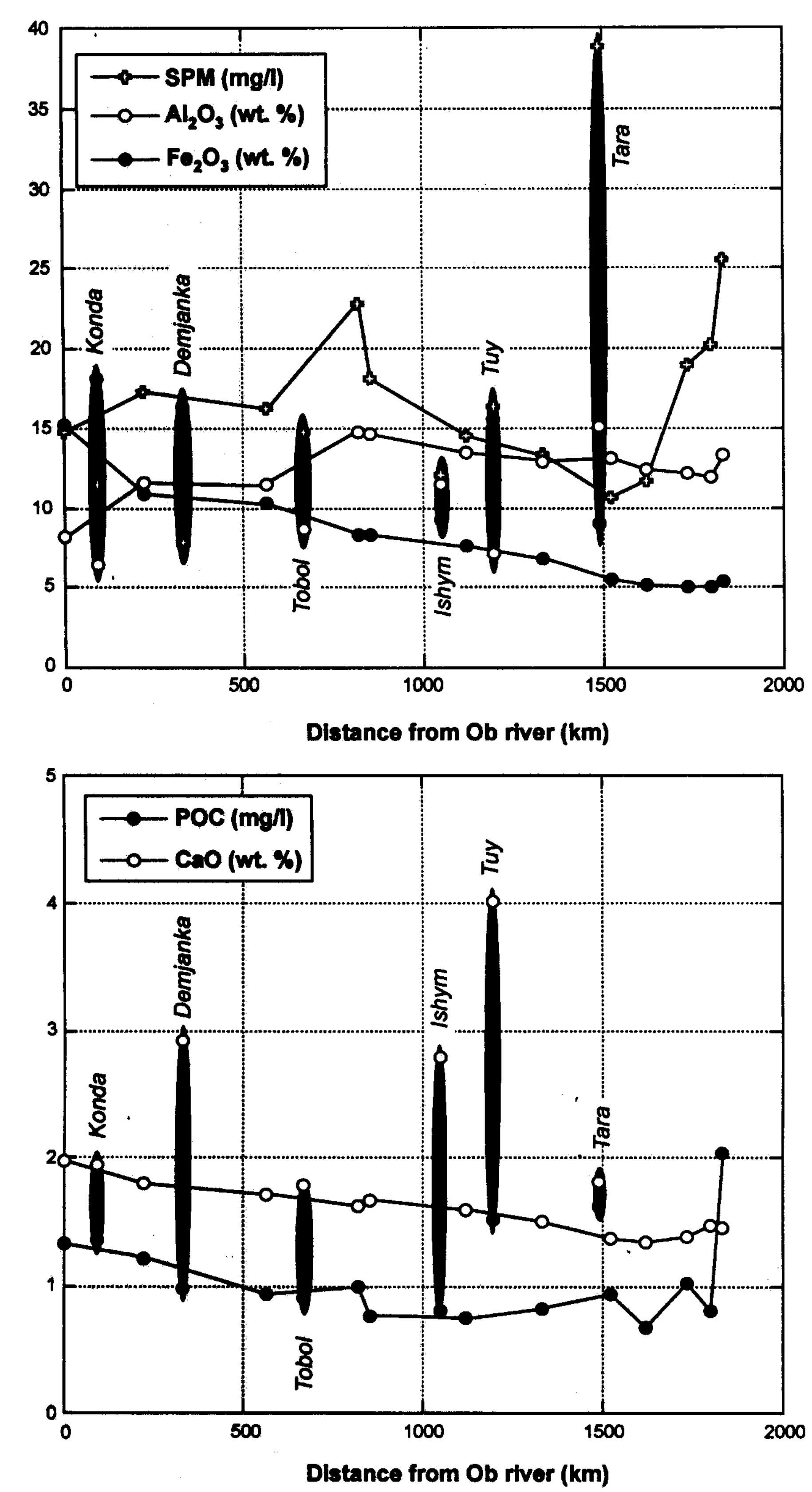


Figure 36 Variations of SPM, Al_2O_3 and Fe_2O_3 (top) and POC and CaO (bottom) in SPM along the Irtysh River. Shaded vertical bars mark concentrations in the tributaries (Gordeev et al., 2004).

That shows that the inflow of the brown coloured tributaries changes the Irtysh SPM composition drastically. As shown in section 4.2.1.4., the concentration of dissolved metals changes as well.

Fig.37 shows the ratios of Al_2O_3 / Fe_2O_3 in SPM. The behaviour of these two oxides is the key in understanding the factor controlling the SPM geochemistry of the Irtysh River. Based on the chemical characteristic, the samples can be divided into three groups.

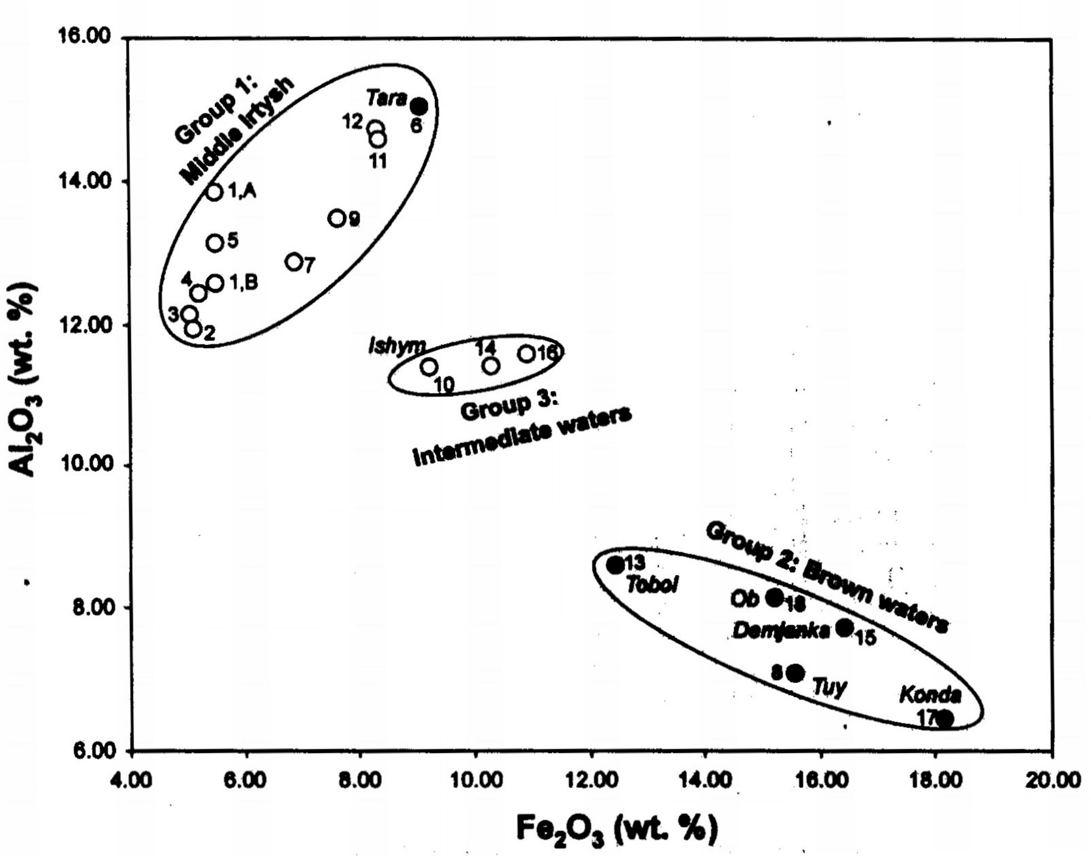


Figure 37 **Interrelations between Al_2O_3 and Fe_2O_3 in SPM of the Irtysh River and its tributaries. Group 1: SPM of middle Irtysh including Tara River; Group 2: SPM of tributaries with brown water; Group 3: mixed yellow gray and brown waters (Sts. 14 and 16) including the Ishim River (St. 10) where sampling was performed in the mixing Zone of Ishim and Irtysh waters (Gordeev et al., 2004).**

Group 1 includes the samples of station 1, 2, 3, 4, 5, 7, 9, 11, 12 of the Irtysh and station 6 of the Tara River. Here, a direct correlation between Al and Fe occurs. The Fe/Al ratio of 0.61 is typical for silicate rocks. The highest Fe_2O_3 and Al_2O_3 were found in the Tara SPM - 9.03% and 15.08% respectively. But composition of the Tara River SPM (St.6) does not differ from that of upper Irtysh SPM.

Group 2 comprises all samples of the brown coloured tributaries Tobol, Demjanka, Tuy, Konda. These samples show a negative Al_2O_3 / Fe_2O_3 ratio.

The samples of station 14, 16 and 10 belong to Group 3 which occupies the intermediate position between Groups 1 and 2. The samples show no correlation between Al and Fe.

It is necessary to note that St. 10 (Ishym River with brown water) was collected in the mixing zone between Ishym and Irtysh Rivers. Therefore St.10 plots in the field of Group 2 (intermediate waters).

The existence of brown coloured water is very common in the western part of the basin between Irtysh and Ob Rivers. This is due to a huge swamp system (approximately 800x350 km) in this area. The level of swampiness reaches 50-80% and reed overgrowths are the dominating type of vegetation in these swamps (Panina, 1972).

The comparison of SPM in the middle Irtysh with that of the brown coloured tributaries (Table 19) reveals that brown coloured water SPM is characterized by a significant higher content of POC (in 1.67 times), P_2O_5 (3.52), Fe_2O_3 (2.55), CaO (1.7) As (2.39), Sr (1.36), Ba (1.18). In contrast, total SPM (0.57), Al_2O_3 (0.58), K_2O (0.54), MgO (0.65), Na_2O (0.60), TiO_2 (0.65), MnO (0.80), and trace metals Cd (0.58), Zn (0.65) show lower concentrations.

The average SPM composition in the lower course of the Irtysh River (so-called "representative Irtysh") represents a mixture between typical silicate material and SPM of brown coloured tributaries.

The major and trace element concentration of middle and "representative" Irtysh SPM in comparison to average age shale (Wedepohl, 1995) are shown in Fig. 38. The values are Al-normalized to compensate for dilution by organic material. Except for some elements (P, Cd, As) a general agreement of the chemical composition of the middle Irtysh SPM (of alumo-silicate composition) and world average is observed. The SPM of the lower, "representative" Irtysh, on the other hand, shows more pronounced deviations, especially an elevated Fe/Al ratio.

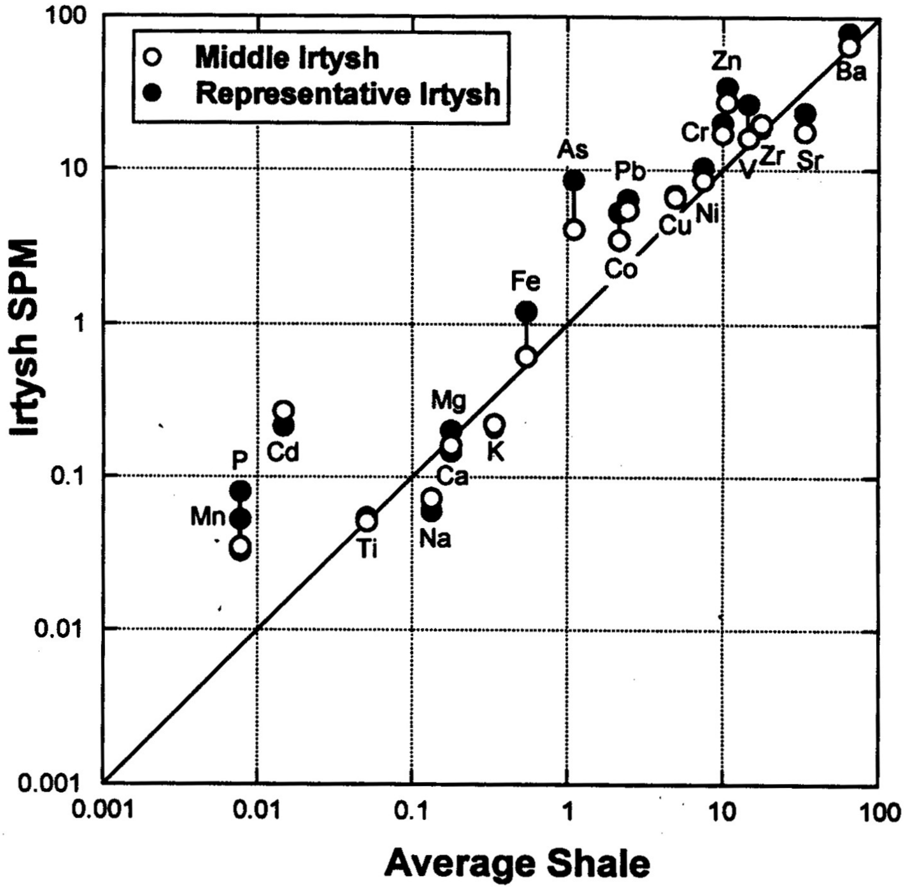


Figure 38 **Average chemical composition of SPM from the middle Irtysh River (below Omsk City) and from the lower Irtysh River ("representative" Irtysh SPM). The x-axis corresponds to the composition of average shale (Wedepohl, 1991). The diagonal represents the straight line of ide3ntical values. Al normalized concentrations based on weight ratio (major elements) and weigh ratios 10^4 (trace elements) are displayed (Gordeev et al., 2004).**

It is a well-known fact that Al, Fe and Mn oxides and oxyhydrates as well as organic matter and carbonates are the most important carriers for trace elements in river SPM. Fig. 39 shows the positive correlation between Fe_2O_3 and POC in brown coloured water SPM. The negative correlation between Al_2O_3 and POC testifies the absence of any Al-organic compounds in SPM of this type of water. Mn does not show any correlation with POC.

After filtration of brown water through nucleopore filters with 0.4 µm pore size, the filtered water practically looses its brown colour. This fact, coupled with the relation between Al_2O_3 and Fe_2O_3 (Fig. 37), indicates that amorphous Fe-organic (Fe-humic) particles are responsible for the brown colour. This evaluation (through Fe/Al ratio) indicates that about 80-85% of Fe in brown water SPM is presented in amorphous form.

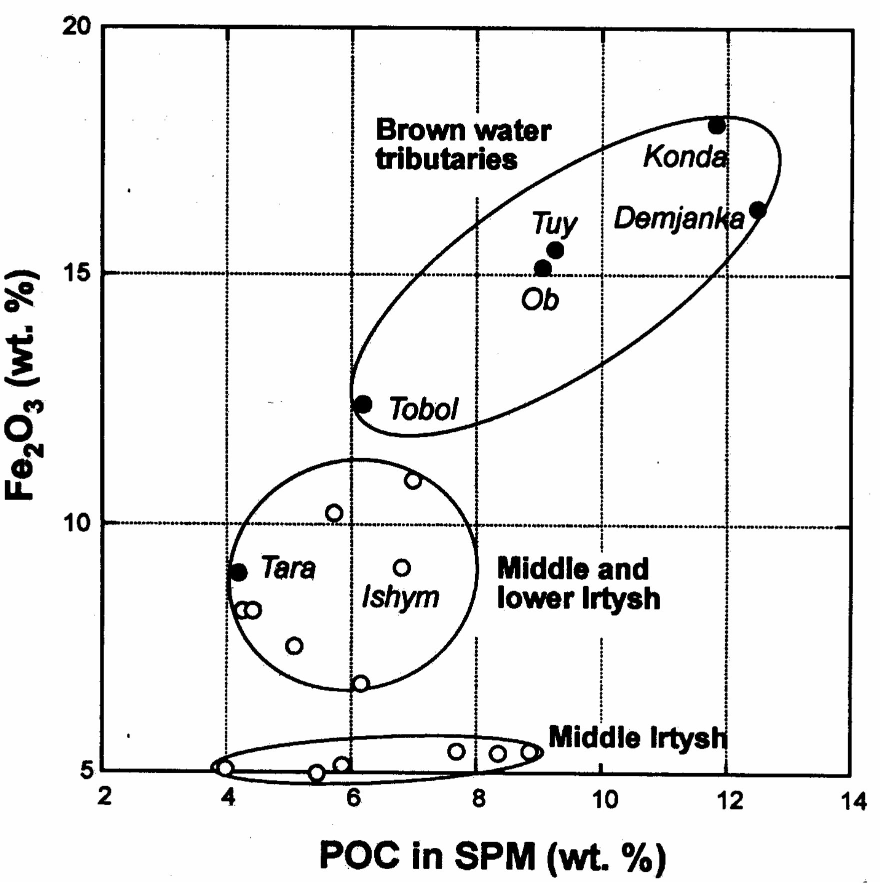


Figure 39 **Correlation between Fe_2O_3 and POC in SPM of the Irtysh River and its tributaries (Gordeev et al., 2004).**

To evaluate the role of swamp peat in the formation of SPM in brown water tributaries, the average composition of peat of the West Siberia lowlands (Inisheva and Tsybukova, 1999) has been compared with the SPM composition (Table 20). Although the ratios between two types of peat (upper layer and low-lying layer with significantly different chemical composition) and brown water SPM cannot serve as direct evidence of the peat origin of the elements in SPM, they may show the direction of trends. In general, the composition of brown SPM is closer to that of the low-lying peat. These data indicate that the low-lying peat deposits might be a source of Ca, Sr and to lesser degree of Ba. Unfortunately organic carbon, Al, P, As and Cd were not analyzed by Inisheva and Tsybukova (1999). Considering the higher POC and P_2O_5 contents in brown water SPM in comparison with silicate SPM of the middle Irtysh, it is also likely that the peat deposits may be a source of these components.

It is assumed that acidic conditions of the swamps are responsible for primary migration of some elements including Fe in dissolved form. The concentration of total dissolved Fe in stagnant water at pH=3-4 reaches 17 mg/l (Inisheva et al., 2000). It is likely that during the mixing with waters of the Irtysh tributaries with pH=6.5-7.1 Fe flocculates and transforms into particulate form. It is reasonable to suggest that a part of dissolved Mn co-precipitated with Fe-floccules as the dissolved Mn concentration decreases from brown to yellow-gray waters by about 50 times (Table 21). This transformation is approved by elevated Mn concentrations in SPM of the lower Irtysh (up to 0.41%).

Among the trace metals, As and Cd are significantly enriched relative to the average for global river SPM (coefficient of enrichment up to 16 for As and 3-3.5 for Cd). The reason of this enrichment is different for the two elements – natural for As and anthropogenic for Cd (Gordeev et al., 2004). Fig. 40 shows the direct correlation between As and P_2O_5 in SPM of the Irtysh River and its tributaries (R^2=0.9328). Also a positive correlation (R^2=0.8431) was found between As and Fe_2O_3 (not shown here). Mal'gin and Puzanov (1996) have detected 27-160 µg/g As in meadow-marsh peaty soils of the Altai plains and concluded a As-P affinity in the weathering products of the Irtysh drainage area. The authors suggest that the main portion of P and As in the acid swamp waters originates from natural phosphate deposits and not from anthropogenic input. Gordeev et al. (2004) concluded that dissolved and colloidal Fe-organic compounds flocculate during the transport from swamp waters to brown and yellow-gray river waters and hereby adsorb dissolved P and As. This positive correlation between As and Fe-POC-P approves the natural sources of As in the SPM of brown water and later in the Irtysh water.

In contrast, Cd is not correlated with P_2O_5. The marsh soils in the taiga zone are characterized by low Cd content with an average of 0.17 µg/g (Polyakov, 1996). The Cd concentration is highest in SPM downstream of Omsk City - 3.6µg/g and slowly decreases to 0.7-0.9 µg/g in a distance of about 700 km. It remains on this level down to the confluence with the Ob River (Fig. 41). The average Cd concentration in the Ob SPM is 0.55 µg/g (Table 17). Most probably the sewage of the large industrial centre Omsk city is responsible for the Cd enrichment of the Irtysh SPM.

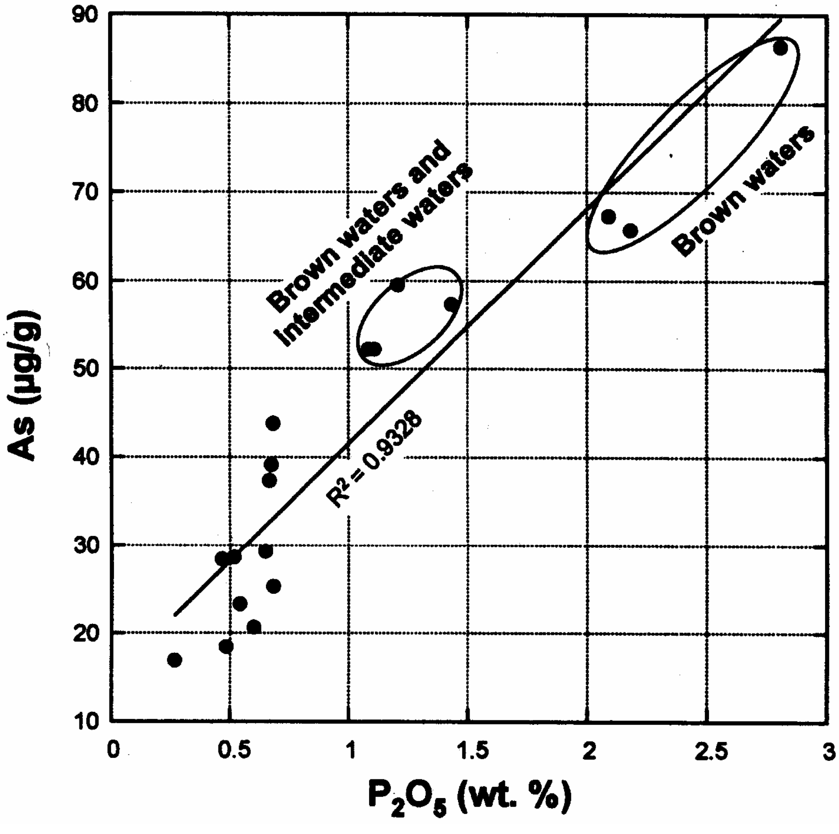


Figure 40 Direct correlation between P_2O_5 and As in SPM of the Irtysh River and its tributaries (Gordeev et al., 2004).

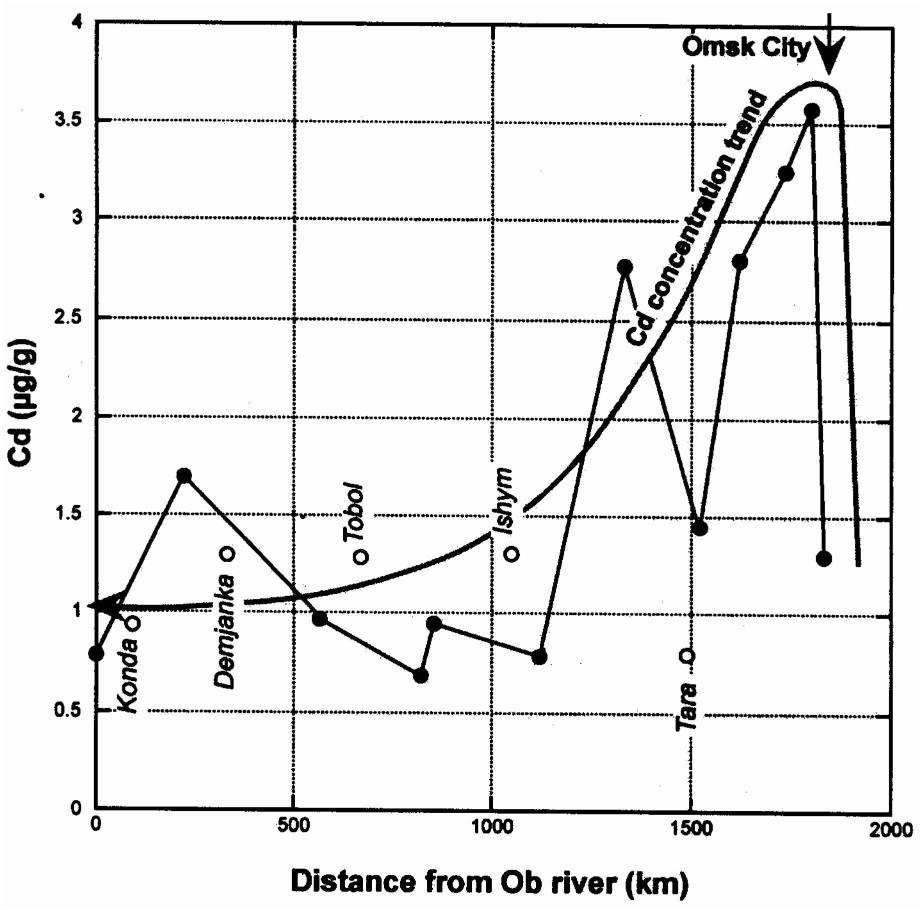


Figure 41 Cd variations in SPM along the Irtysh River (Gordeev et al., 2004).

4.2.3 Gross river fluxes to the Arctic Ocean

4.2.3.1 Major ions

Multi-annual average on major anions, exported in dissolved form, and major cations, exported in dissolved and particulate form, are shown in Table 22.

The annual chemical denudation rate for Ob, Yenisey and Lena basins are 19.5, 23.9 t/km^2 and 23.4 t/km^2, respectively. This is about half of current annual world average (36 t/km^2, Meybeck, 1979). The variations in anion and cation discharge (monthly average) in the course of a year are illustrated exemplarily on the Lena River (Fig. 42). Noticeable features are the strong fluctuations in Ca and HCO_3 discharge simultaneously with changes in the water runoff. In contrast, small variations of the discharged Na+K and Cl occur. In the work of Gordeev and Sidorov (1993) it was shown that the ground waters in the Lena basin were highly concentrated (10-20 g/l) and total Na+K constituted 95-97% of the sum of cations while among the anions Cl has predominated (more 95%).

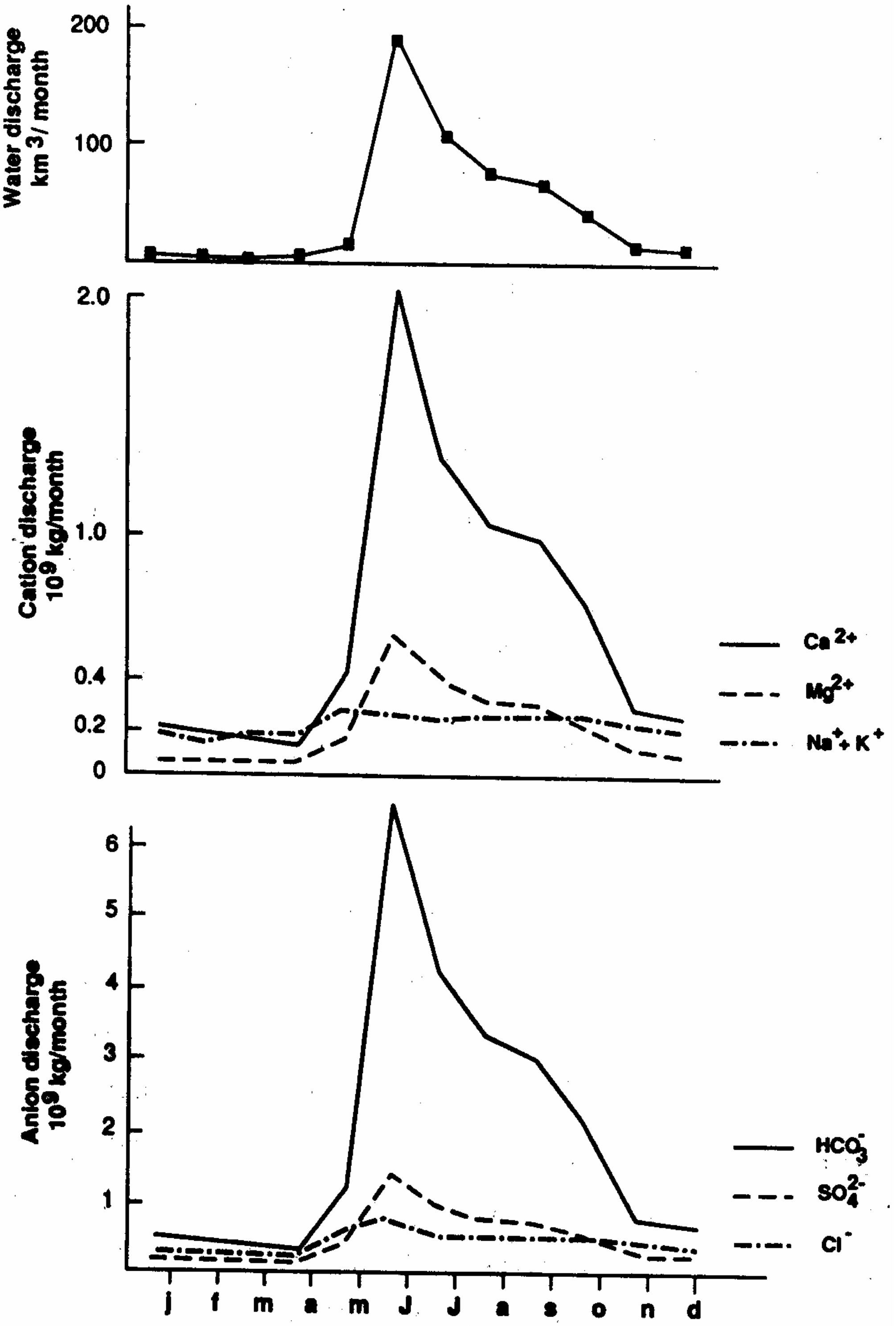


Figure 42 Average monthly multi-annual cation and anion discharge variations in the course of a year in the Lena River (Gordeev and Sidorov, 1993).

Fig. 42 shows a roughly constant discharge rate of ground water during the year. In spring and summer a steep increase of water discharge is caused by snow melt and atmospheric precipitation. The relatively small inflow of Cl-Na ground waters is suppressed by this abundance of water. During the winter, when the water discharge diminishes by three orders of magnitude, approximately the same volume of groundwater is released into the river. It is reasonably to assume similar pattern of seasonal variations of cation and anion discharges in Ob and Yenisey.

4.2.3.2 Dissolved, particulate and total organic carbon (DOC, POC and TOC)

The most reliable estimates of DOC, POC and TOC export for Ob and Yenisey were obtained in the work of Kohler et al. (2003). The authors estimated annual DOC fluxes for both rivers by multiplying the multi-annual monthly average water discharge for the period 1980-1999 on measured and estimated DOC concentrations of the corresponding months. The summer period (June-September), which contributes about 70% of the organic carbon discharged in the Ob and Yenisey, was covered well by their own data set. The winter (November-April) and pre-flood DOC values were adopted from literature data (Table 23).

Seasonal variations of DOC fluxes for the Ob and Yenisey Rivers (Fig.24) show that freshet accounts the major part of the annual DOC discharge of both rivers while the total winter DOC export is significantly lower. The comparison to the Lena River (Cauwet and Sidorov, 1996) clearly indicates that the proportion of organic matter, transported during freshet, increases from west to east (Ob<Yenisey<Lena) (Gordeev and Rachold, 2003).

4.2.3.3 Nutrients

Holmes et al. (2001) demonstrate that multi-annual data of Roskomhydromet on NO_3, PO_4 and SiO_2 concentrations in the Russian Arctic river were reliable, whereas NH_4 data show analytical errors. Therefore the assessments on annual NO_3 and PO_4 fluxes can be considered acceptable. For Ob, Yenisey and Lena the periods 1986-95, 1985-95 and 1984-95 were investigated. The results are given in Table 24 in comparison with previous estimates (Gordeev, 2000).

Attract attention very high fluxes of organic forms of dissolved N and P in comparison to the fluxes of their inorganic forms.

Very preliminary estimates of the particulate organic nitrogen (PON) and particulate organic phosphorus (POP) fluxes show that they are of the same order as the fluxes of inorganic NO_3 and PO_4.

4.2.3.4 Major dissolved and particulate elements

The flux of particulate and dissolved major elements of Ob, Yenisey and Lena is summarized in Table 25. The average element concentration and multi-annual discharges of water and suspended sediment were employed to calculate the flux.

The fluxes of Na, Ca, K and Na in dissolved form are significantly higher than that in suspended matter. The opposite situation is observed for the fluxes of Si and Fe (and probably for Al and Ti the data for those in dissolved form are absent). The flux of dissolved Fe is less than 5% and of dissolved Si 20-30% of their total (dissolved and particulate) fluxes.

In this aspect, the Yenisey River differs from Ob and Lena. Due to its very low sediment discharge, the Fe flux in dissolved form is relatively higher compared to Ob and Lena, and the Si flux in dissolved form even dominates over the particulate flux.

4.2.3.5 Trace dissolved and particulate elements

Here, new gross estimates of the flux of trace metals into the Arctic Ocean are presented. They are based on average concentrations of dissolved (Table 8) and particulate (Table 17) forms of trace elements in the lower courses of Ob and Yenisey (Table 27). These calculations are slightly higher than previous estimates of Gordeev (2002) because new results for the Ob River in the winter period have been included. As shown in section 4.2.1.4, almost all metal concentrations appear to be higher in winter than in summer and autumn. Data for the period of the highest water discharge in spring, when most of the elements are delivered into the ocean, are lacking. Data are difficult to obtain, as the great ice-flow at the time of maximum discharge prevents field works.

4.3 Estuarine processes in water column

An estuary is defined as a place where a river meets an inlet of the sea (Fairbridge, 1980). The mixing zone of fluvial water and seawater is an arena of a variety of physical, chemical and biological processes which may lead to dramatic quantitative and qualitative transformation of riverine sedimentary material.

The zone is termed "marginal filter" by A.P. Lisitzin (1994, 1998). The model of marginal filter is shortly presented here for a better understanding of the processes in Ob Guba and Yenisey Bay.

4.3.1 The marginal filter (MF) model

The marginal filter consists of two main parts, which differ principally in their function:

1) abiotic part, situated close to the river mouth, and

2) biotic part, located offshore, seaward (Fig. 43 A).

The abiotic, terrigenous part of the filter includes three sequential steps:

Step I. coarse-grained

Step II. fine-dispersive

Step III. physico-chemical (or newly formed sorbents).

The biotic part of marginal filter consists of two key steps:

Step IV. Phytoplankton pump

Step V. Zooplankton pump.

The model is a strong simplification of the processes in the mixing zone between river and sea. All five steps are sequential, with increasing of salinity from the river end member to the sea end member. The borders between the marginal filter steps are not sharp.

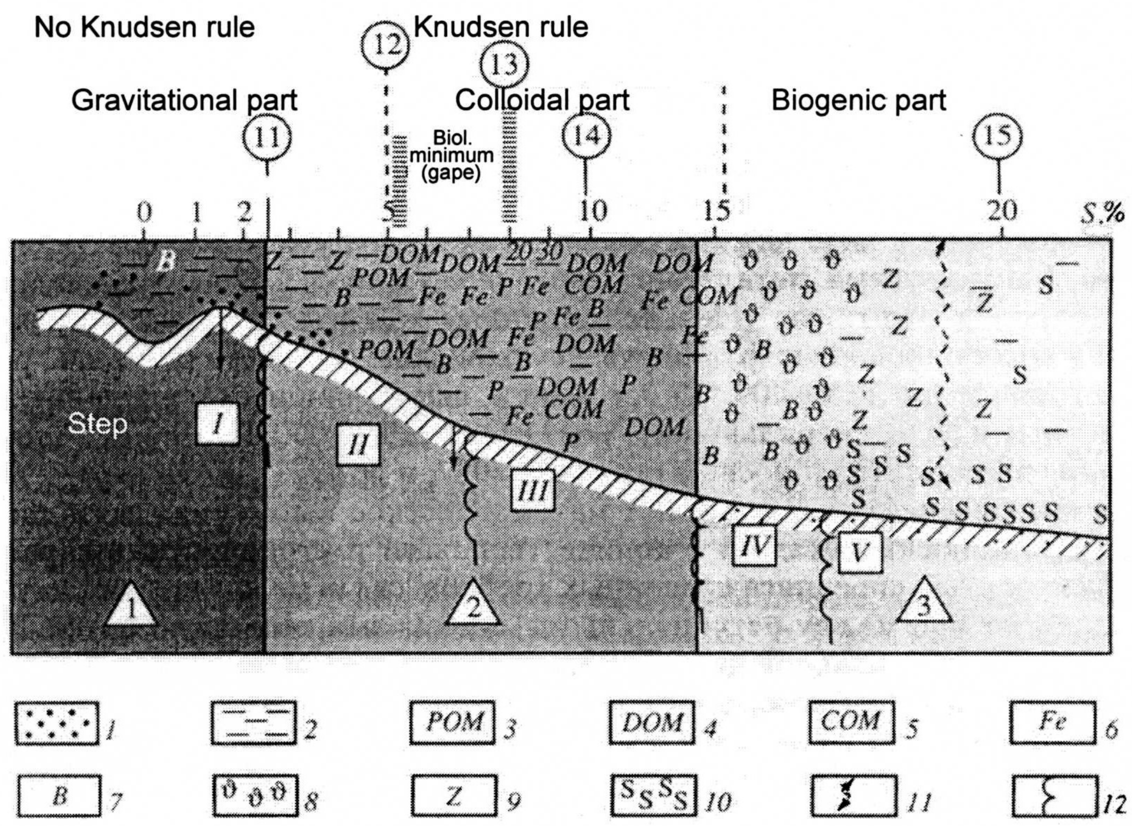


Figure 43(A) Model of marginal filter (MF) quantitative parameters of its work (Lisitzin, 1999).

Abiotic parts of the filter (steps I and II), 1 - settling out of coarse fractions in SPM (sands and silt aleurites), 2 - settling out of fine (pelitic) fractions of SPM; Physico-chemical part of the filter (step III), 3 - settling out of terrigenous particulate organic matter (POM), 4 - settling out of terrigenous dissolved organic matter (DOM), 5 - coagulation and flocculation of colloidal organic matter (COM), 6 - Fe-oxyhydrate sorbent and complex (OM + Fe + clay minerals) sorbent formation; Biotic parts of the filter (steps IV and V), 7- spread of bacterioplankton, 8 – area of maximum phytoplankton development (phytoplankton biopump), 9 - area of development of zooplankton filter organisms (zooplankton biopump), 10 - flux of pellets, t.i. transfer of fine particles by zooplankton (selectiveless filtration) into bottom sediments, 11-12 - depocentres of different parts of MF: 11 - gravitational and colloidal (coagulational), 12 - biological and pelletic. At bottom - phytoplankton biopump-1, zooplankton biopump-2, benthos and macrophytes biopump-3.

Abiotic parts of MF

Step I. The coarse-grained part of the filter

Step I occurs at the mouth and adjacent part of estuary. The sediments consist of particles larger than 0.01 mm (mineral grain fragments, sands and aleurites, terrestrial plant remains such as peat, wood, etc.). The mineral grains have generally a coat of organic matter and Fe oxyhydrates that retain some dissolved forms of elements and transfer them to bottom sediments.

Lisitzin considers that at the first step of the Arctic marginal filters up to 50% of total fluvial particulate matter is deposited.

Step II. The fine-grained part of a filter

The fine grained fraction of the SPM (<10 μm) gradually replaces the coarser one as the river water flows seaward.

The pelitic fraction, like all particles of natural suspensions in aqueous medium, has a negative charge. Coagulation of fine particles in river suspended matter is of major significance under the effect of an electrolyte (sea water). Under conditions of massive coagulation the "silt plug" arises where suspended matter concentration is even higher than those of the original river water. It is a zone of maximum sedimentation rates.

High concentration of suspended matter restricts phytoplankton development, even where nutrient levels are high, due to deficit of solar radiation. The biotic processes are therefore negligible here.

The sediment fluxes at step II of the Ob and Yenisey marginal filters have been measured in late summer of 1993. The values were 1.32 and 22.1 g/m^2 per day, respectively while in the outer parts of the estuaries and in adjacent area of the Kara Sea the typical fluxes were between 0.001-0.02 g/m^2 per day (Lisitzin et al., 1994).

Step III. The physico-chemical part of MF: the colloidal pump (C-pump).

The colloidal system consists of clay minerals (abiotic part) and living picoplankton and excretory products- bacteria, viruses, coccolithophors, etc. (biotic part). 1 ml of saline water contains about 10^9 colloidal particles with total surface area about 8 m^2 (Lisitzin,1998).

In the salinity range between 3 - 20‰ massive flocculation of dissolved organic matter, Fe, Mn and Al oxyhydrates takes place. These freshly formed floccules are very powerful sorbents that selectively capture elements from solution. The process of flocculation has been confirmed in experiments with river and seawater mixing by Sholkovitz (1976).

The ion-exchange reactions occur in the mixing zone (sorption-desorption processes). There are the key exchange reactions with replacement of some ions on the particle surfaces. This is the main difference to step I and II: the sorbents here are formed in situ from solution while they were released from terrigenous material (soils and weathering crust) at steps I-II.

A re-packing of trace elements from river suspended matter into fresh floccules takes place in this stage.

OM, dissolved and colloidal, plays a highly important role at this and the following step IV. OM is not only the most significant sorbent but it also determines many other mechanisms of the MF operation such as the precipitation of major part of dissolved Fe.

In Ob and Yenisey Estuaries and in the Kara Sea the formation of OM floccules is associated with nutrition of bacteria and zooplankton that transformed dissolved OM into floccules. In the copepods stomachs from the marginal filter almost only floccules (not phytoplankton, as is generally the case in a biological part of MF) were found (Lisitzin, 1998). Hence, DOM enters the zooplankton food chains via floccules and bacteria.

At this stage water is usually still turbid as active phytoplankton growth. Here physicochemical rather than gravitational laws are dominant. It is a so-called "colloidal pump".

Biotic parts of MF

There are several key features of the biotic parts of the MF.

Dissolved chemical elements are involved here in the biological cycle and incorporated into cellular tissue, tests and metabolites losing the chemical properties (i.e. in chelated compounds). Only after decomposition of organisms and their organic residues, the elements recover their chemical properties again.

Another specific feature of the biotic parts of MF is the biological concentration of dissolved elements by organisms. As a result, the composition of organisms differs radically from that of water in which they live.

Phytoplankton performs very important geochemical changes in the estuarine zone. It transfers dissolved elements into suspended particles. At last, zooplankton and benthic organisms are able to filter the whole estuarine water volume transferring the remaining suspended matter, including newly formed floccules into the large clumps which deposits to bottom sediments.

Step IV. The phytoplankton part of MF

At this stage (salinity between 3 and 10‰), mineral suspended particles and colloids are already removed, the water transparency increased, the nutrients concentration high, and the phytoplankton bloom takes place. This biological pump captures dissolved material, transforms it and transports to the bottom. The key regulating factors are the rates of primary production and the available biomass.

Phytoplankton biomass is also “self-limited”. Due to very high number of the organisms water transparency decreases and despite of high nutrient concentrations no further increase of biomass occurs. The "biological plug" is formed by organic particulate matter and is found near the "silt plug".

At step IV, as opposed to the first three steps, phytoplankton biomass is limited also by zooplankton grazing. This may lead to very significant reduction of phytoplankton biomass. Large amounts of OM are autochthonous, newly formed phytoplankton organisms, mainly marine species. Dead and dying cells and organic matter serve as additional powerful sorbent which may extract the remaining dissolved elements from water.

The influx of fresh OM causes the growth of zooplankton and benthic and nektonic organisms. The benthic organisms present the final step of biofiltration of material already filtered by zooplankton.

Step V. The zooplankton part of MF

Zooplankton organisms filtrate both biotic and terrigenous particles, pack them in large size pellets and transport them to the bottom. This pellet flux without substantial alteration may reach the bottom within 24 hours Lisitzin (1998). The daily demand of zooplankton for food is about 50-70% of their weight. An average POC in surface layer in the estuaries is about 20%. To obtain an adequate ration the zooplankton organisms have to filter 2-5 times their body weight per day. Taking into account that typical mesoplankton biomass in the estuaries exceeds 1000 mg/m^3 of water, they need to filter at least 2000-5000 mg of suspended matter per day. In September 1993 (49 cruise of R/V "Dimitry Mendeleev") the maximum concentration of suspended matter in both estuaries was about 5 g/m^3. So, in order to satisfy its food requirements, zooplankton has to filter the whole water volume of the estuaries within 1-2 day only.

Specific features of MF in the Arctic.

The MFs in the Arctic estuaries have their specific features defined by climatic, geographic and geological conditions of the region. Shortly, they are concluded in the following:

- low thickness of weathering crust in the huge catchments of the Arctic rivers and as the result is weak washing of sedimentary material and low SPM fluxes;
- sharp seasonal variability of water and SPM discharges, very significant difference between MF's work at summer and winter periods – MF's are much more active in summer time;
- penetration of fresh waters under ice cover for a long distance if to compare to the period of ice absence;
- sinking and distribution along the deeps on the ocean bottom of heavy saline waters formed during ice formation.

The MFs of the Ob and Yenisey Rivers are shown in Fig.43 B (Lisitzin, 1998).

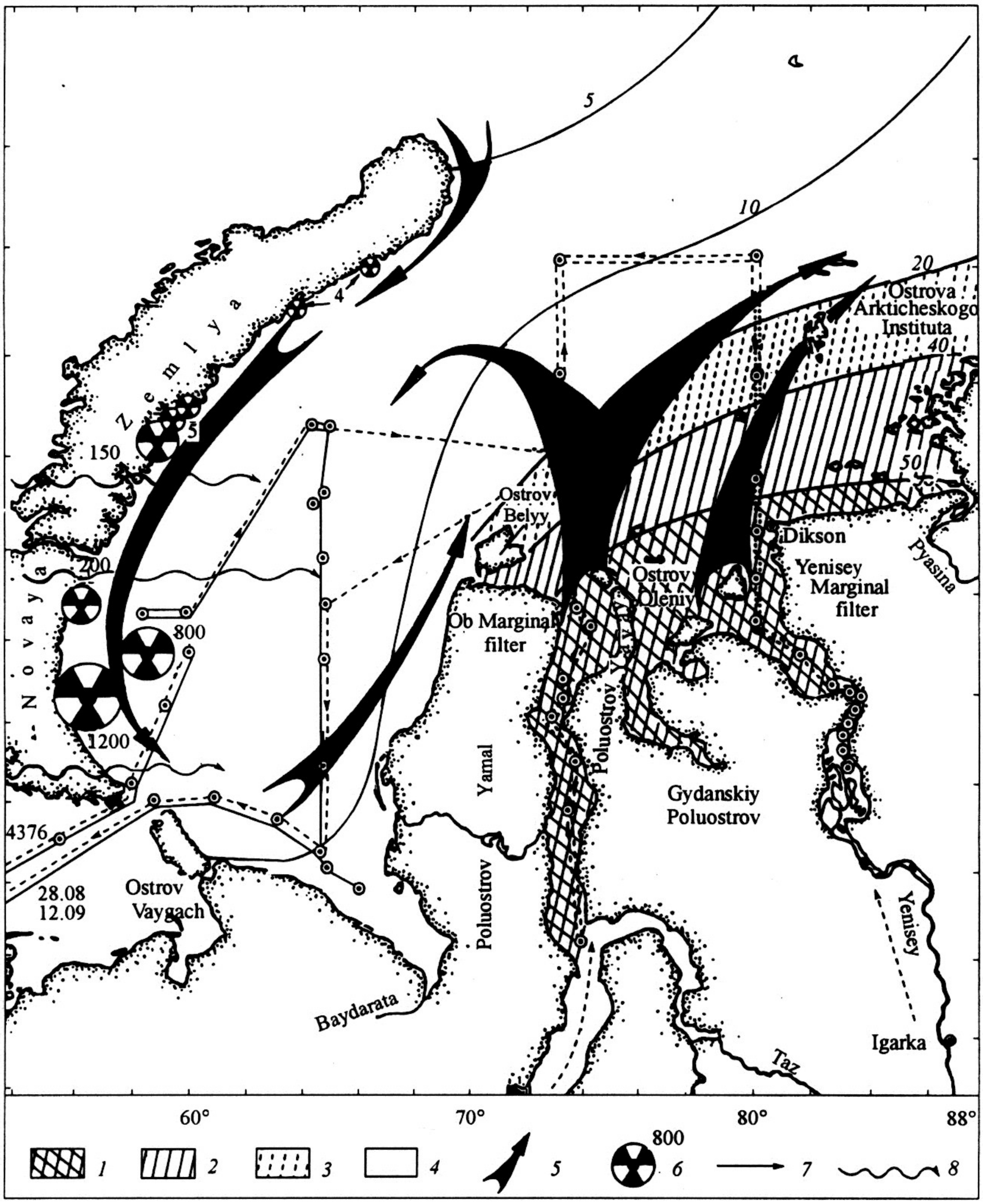


Figure 43(B) Marginal filter action scheme for the Kara Sea and the major sources of pollution (Lisitzin, 1994). Propagation distance of river water (according to the multiannual average silicate distribution in surface water): 1 > 50, 2 - 40-50, 3 - 20-40, 4 < 20 µM Si, 5 - main directions of sea and river water transport, 6 - largest areas of solid radioactive waste dumping and possible pollution of deep water (numbers denote activity), 7 - supply of dissolved and suspended nuclides from rivers, 8 - the main transport directions of aerosol material of the nuclear explosions of Novaya Zemlya (mean summer wind directions). The route and stations of the 49-th cruise of the R/V "Dmitry Mendeleev" are shown.

Concluding remarks on MF

The proposed MF model includes 5 steps, with a set of consequences. Each step has its own characteristic and locality associated with salinity, nutrients and other factors.

The model changes with environmental conditions and some steps may overlap or undergo seasonal variations. The importance of each step depends on climatic zones and changes within seasonal and inter annual cycles.

The general direction of the process in the estuarine zone is massive transfer of matter (suspended particulate, colloidal and truly dissolved forms of elements) into the bottom deposits.

Previous studies (Gordeev, 1983; Lisitzin et al., 1982; Lisitzin, 1994) have shown that the continent-ocean marginal filter could remove more than 90% of particulate matter and 20-40% of dissolved substances from water and transform most dissolved forms into particulate suspended matter and transport it to the bottom.

However, the model has some limitations. One of them is that the mixing processes are considering without impacts produced by tides, offshore and onshore winds and waves.

Lisitzin's final phrase was: "If the most talented engineer tried to create such a perfect water purification system, all parts of which are interacting both in space and time, he would fail! It will not be an exaggeration to say that the system of marginal filters, which we are just beginning to understand, is one of the nature wonders".

4.3.2 Dissolved elements in MF

4.3.2.1 Major ions

Major cations and anions in river waters behave conservatively in the mixing zone, they overcome the MF without losses (Liss, 1977; Gordeev, 1983; Chester, 1990). There are only few cases when the major cations demonstrate non-conservative behaviour. For example, dissolved Ca and Mg in the Lena River was removed in the salinity range of 0-10‰ (with maximum 3‰) (Tishenko et al., 1999). The authors assume that about 7% of dissolved Ca flocculated as colloidal $CaCO_3$.

In the Ob and Yenisey Estuaries a loss of dissolved Ca, Mg, K, Na as well as dissolved anions HCO_3, SO_4 has not been observed. Several examples of major cations and anions in both estuaries are shown in Fig.44. The concentrations of these elements and components follow a linear trend with increasing concentrations from river to sea that indicate their conservative behaviour.

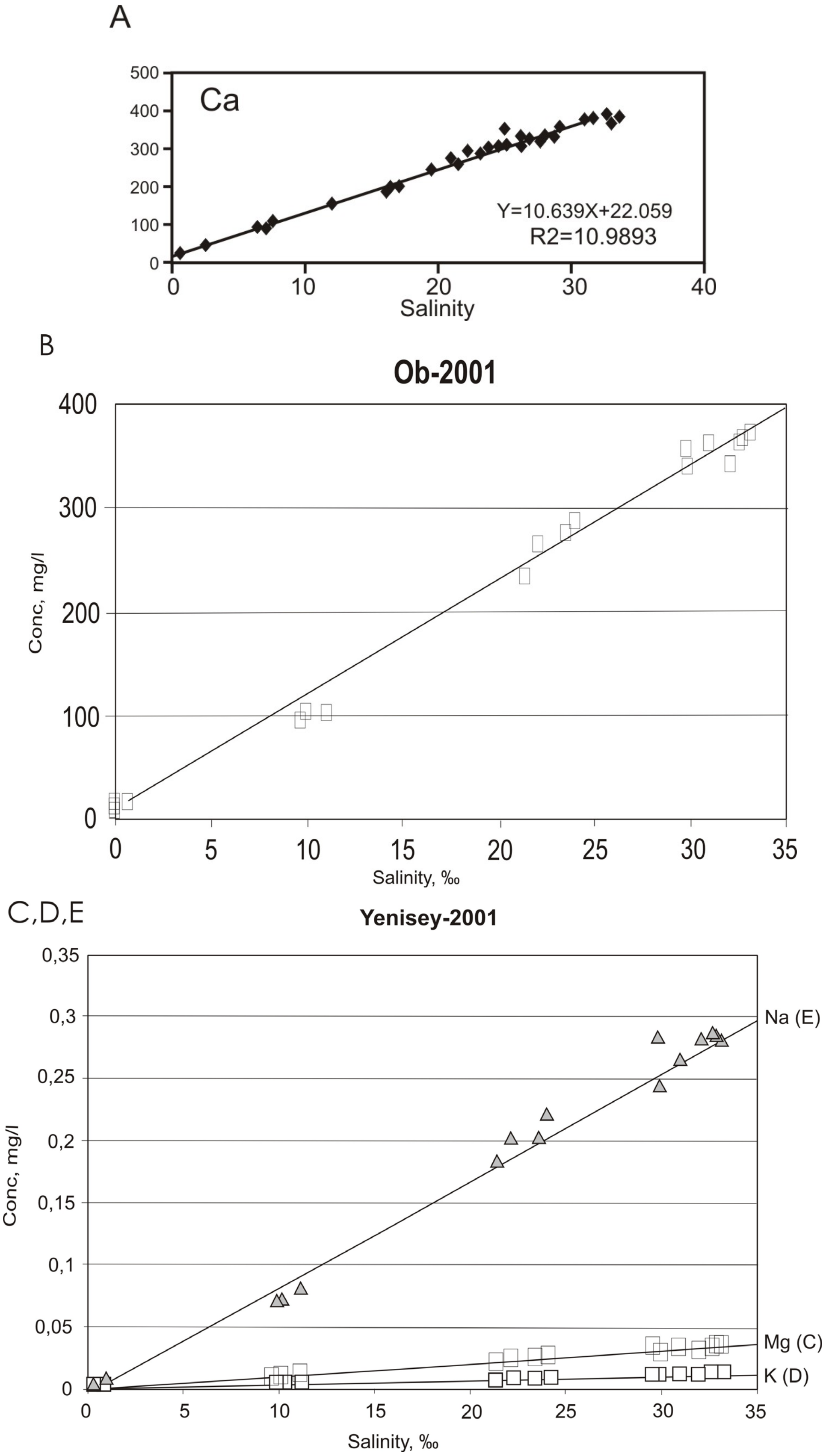


Figure 44 **Conservative behaviour of major cations and anions in the estuarine zones of the Ob and Yenisey: Ca - Yenisey, 2000 (A), Ob, 2001 (B), Na, Mg, K - Yenisey, 2001 (C, D, E), HCO_3-Yenisey, 2001 (F).**

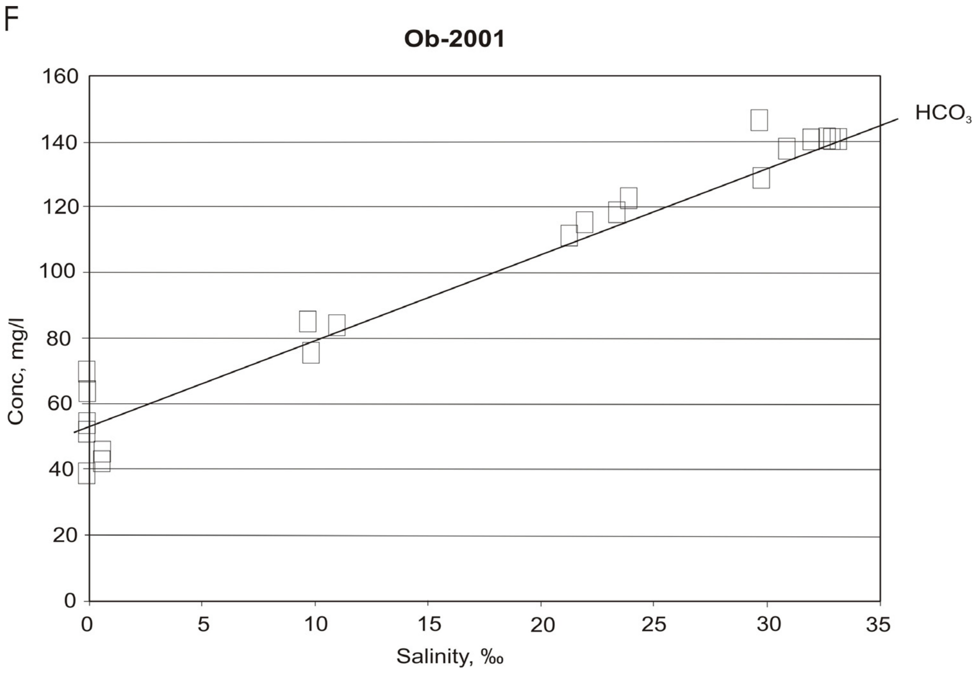


Figure 44 continued

4.3.2.2 Organic carbon (DOC)

Examples of DOC behaviour with increasing salinity in the Ob and Yenisey Estuaries are shown in Fig. 45. The data indicate the conservative distribution of riverine DOC in the Kara Sea. The differences in the slopes of the regression lines reveal seasonal and inter-annual variations in the river end member concentrations.

However, Kohler et al. (2003) consider that the conservative behaviour of DOC does not necessarily exclude the existence of effective removal for river DOC because sources and sinks of DOM on the shelf could be of similar magnitude.

They carried out a mixing experiment with Yenisey water (S=0‰) and open Kara Sea deep water (S>33‰) (Fig.46). This experiment indicated very small DOC loss in the low salinity range (S<5‰) of about 3% relative to the theoretical conservative mixing line with increasing POC concentrations in the same salinity range. However, the minor loss of DOC and small increase of POC were not much above the analytical range of accuracy.

In the work of Dai and Martin (1995) the DOC behaviour in the estuaries of both rivers were also found to be conservative. Pre-filtrated (0.4 µm Nucleopore filters) water was further processed through a cross-flow ultra-filtration system with 10^4 Dalton polysulphate membrane (corresponding to a pore size of ~ 3 nm) to separate colloids from the truly dissolved fraction. The results show that 30-60% of POC in the Ob and 30-45% in the Yenisey was held in the colloidal fraction. And namely this fraction has demonstrated non-conservative behaviour whereas the POC concentration (as a sum of truly dissolved and colloidal fraction) decreased linearly with salinity.

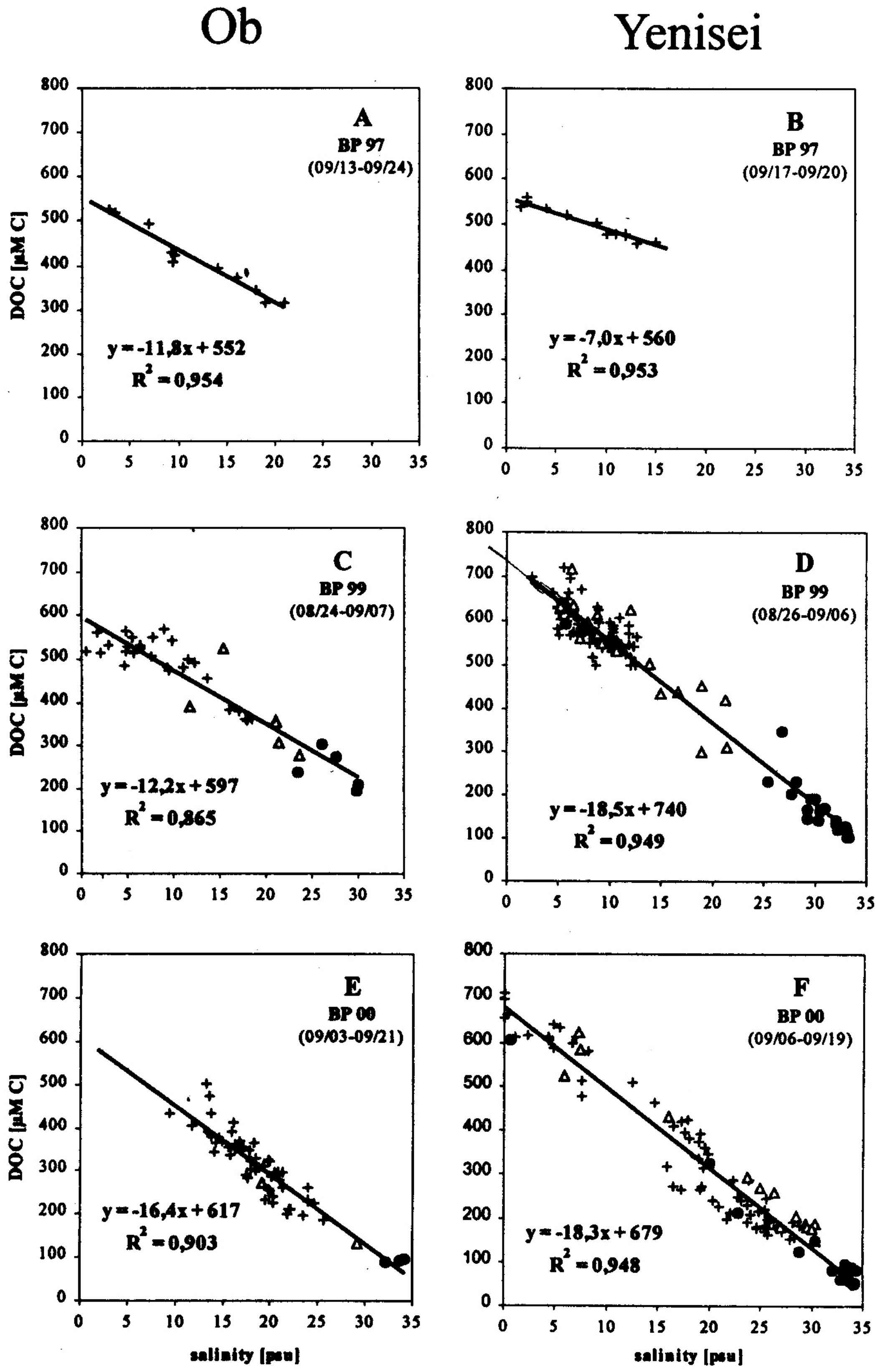


Figure 45 DOC distribution along transect in the Ob (A - 1997, C - 1999, E - 2000) and Yenisey Estuary (B - 1997, D - 1999, F - 2000). Samples are subdivided into surface (+), pycnocline (Δ) and deep (•) samples (Kohler et al., 2003).

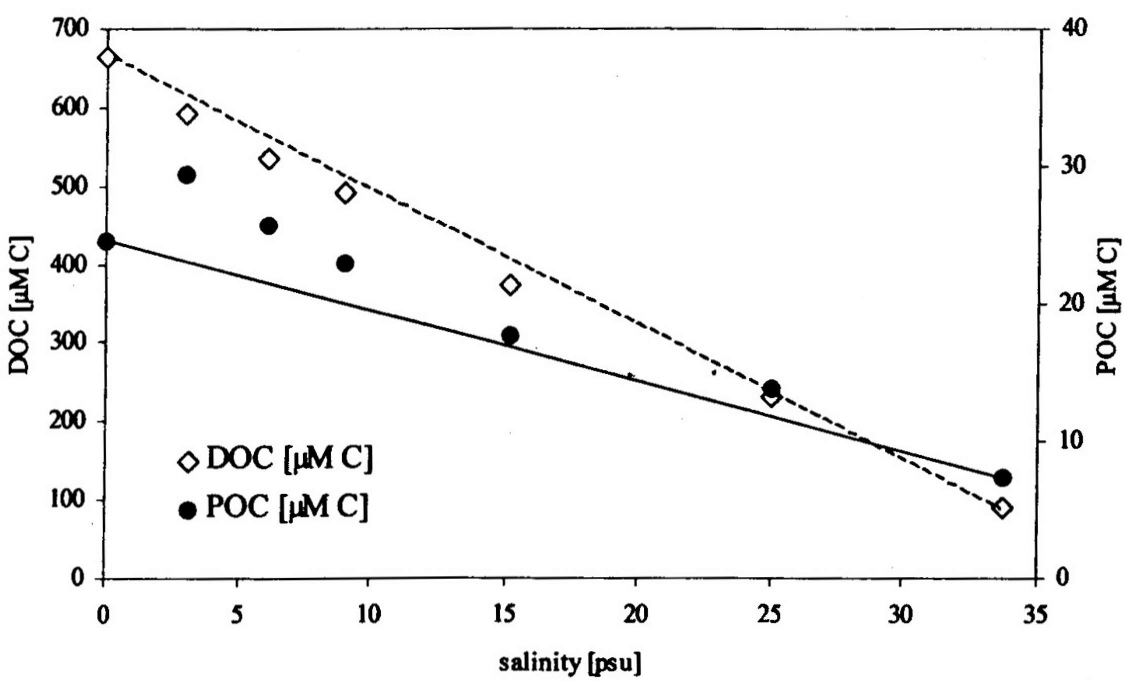


Figure 46 **Partitioning of DOC and POC during mixing experiment of Yenisey water (S=0) and open Kara Sea deep water (S>33‰). The two end members and the 5 mixtures are each represented by one pair of data (Kohler et al., 2003).**

4.3.2.3 Nutrients

The behaviour of dissolved nutrients and silica in the mixing zones of the Ob and Yenisey Estuary were studied by Makkaveev and Stunjzhas (1994) during the 49th cruise of the R/V "Dmitry Mendeleev" in autumn of 1993. Presented in the original paper distributions of nutrients on the river-sea cross-sections with distance from mouth to sea were transformed into their distribution along the salinity gradients (Fig.47 A). As mentioned above, in salinity range 2-5‰ and 15-20‰ two frontal zones with sharp gradients of hydrochemical parameters occur in both estuaries. In near-bottom waters of the first front the values of dissolved O_2 and the pH sharply decreased whereas the nutrient concentrations increased. The bulk of terrestrial organic matter is deposited and oxidized in the sea bottom, nutrient regeneration occurs, and the so-called "biogenic trap" is formed here. The second frontal zone (S=15-20‰) is also characterized by sharp gradients of hydrochemical parameters and nutrient concentrations. On the Ob transect NO_3 and PO_4 concentrations are relatively stable in surface waters, but decreased strongly after crossing the frontal zone. An active consumption of nutrients, high nutrient input and high transparency of the water column are the reasons for this. Regeneration of OM deposited down to near-bottom waters results in high concentrations of nutrients with maximum at salinity 30-32 ‰.

In the Yenisey Estuary, the nitrate concentration was permanently low. This nutrient was probably the limiting factor for primary production (PP) in the estuary. Low NO_3 and high NH_4 demonstrate the active consumption of phytoplankton by zooplankton. PO_4 concentrations show some increase with salinity that may be probably explained by the increasing rate of PO_4 turnover as a result of higher PP and the intensity of OM degradation in near-bottom waters.

The determinations of dissolved nutrients were repeated in the expedition of the R/V "Academic Boris Petrov" in 1997, 1999, 2000, 2001 and 2003. The distribution of NO_3 and PO_4 in the Ob Estuary in 1999 and Si in the Yenisey Estuary in 2000 are presented in Fig. 47 B and C. The results of other expeditions are given in Tables 26 (I-VII).

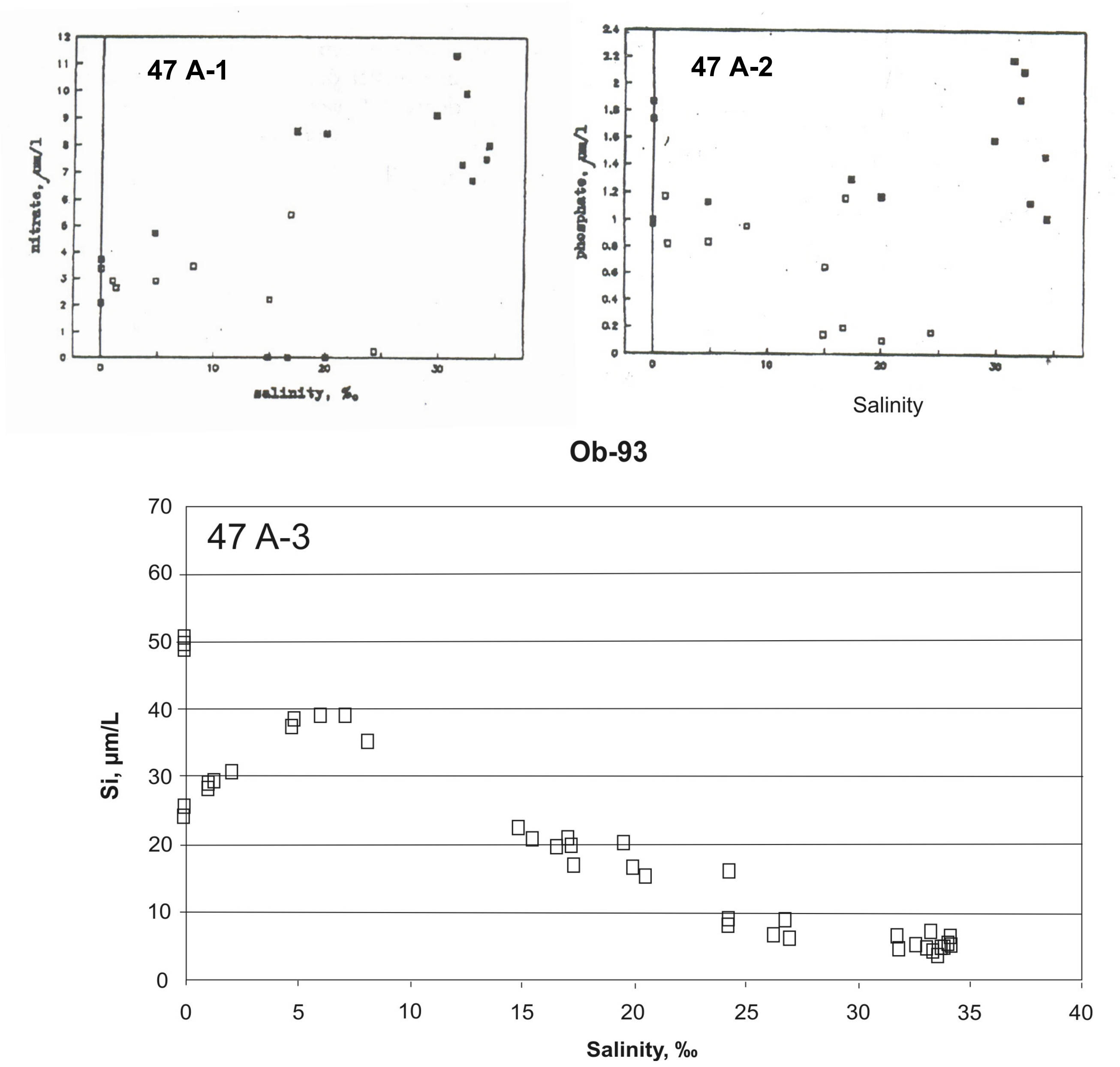
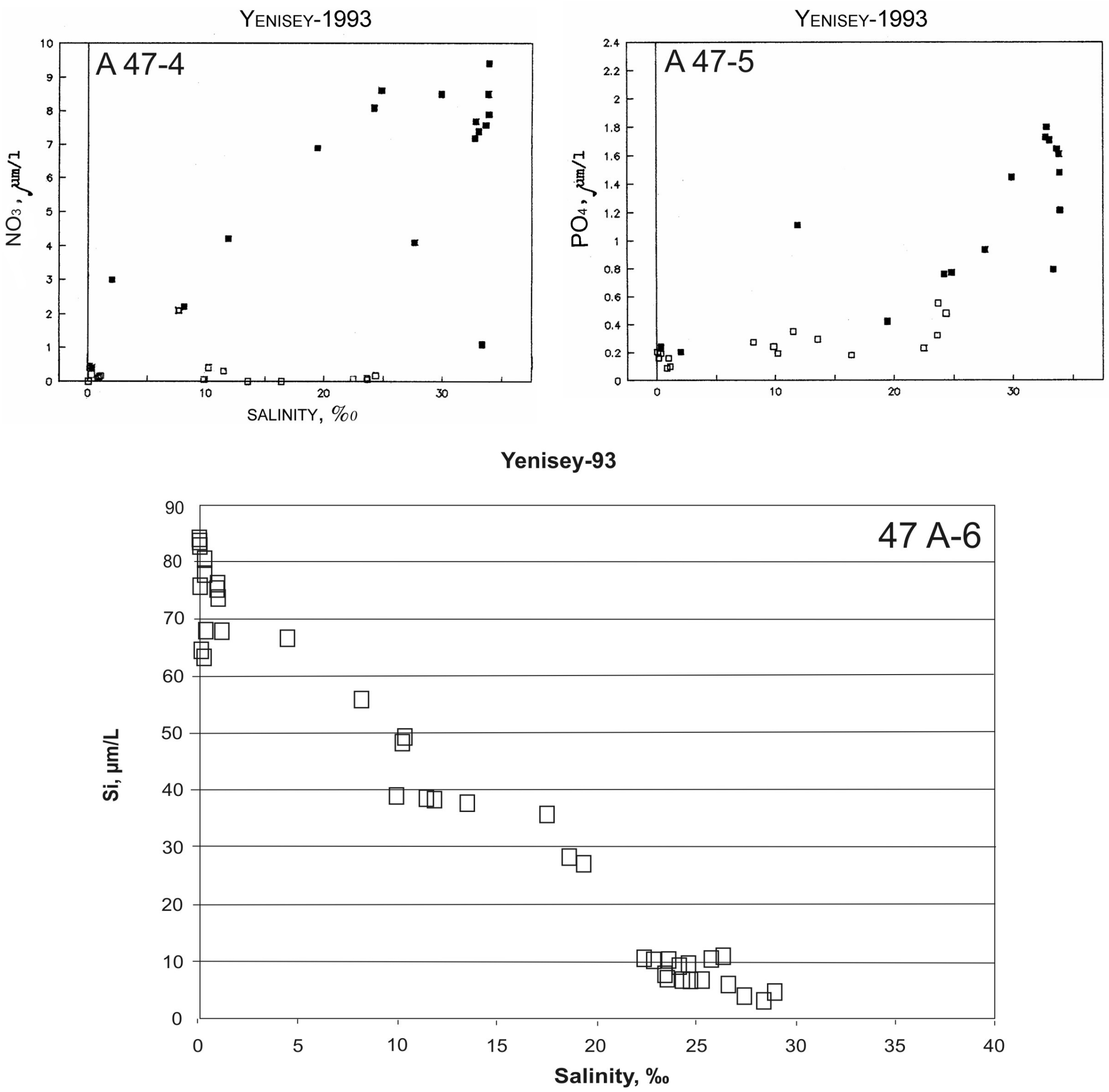


Figure 47 **Distribution of dissolved nutrients in the Ob and Yenisey Estuaries. A, 1993: Ob - NO3 (A–1), PO4 (A-2), Si (A-3), Yenisey - NO3 (A-4), PO4 (A-5), Si (A-6) (Makkaveev and Stunjhas, 1994), open squares- surface and intermediate samples, closed squares- near bottom samples; B, 1999: Ob - NO3 (B-1), PO4 (B-2), Yenisey - NO3 (B-3), PO4(B-4), closed rhombs- surface and intermediate samples, open circles- near bottom samples (Sukhoruk and Tokarev, 2000); C, 2000 - Yenisey (Si), symbols as in (B) (Sukhoruk et al., 2001).**



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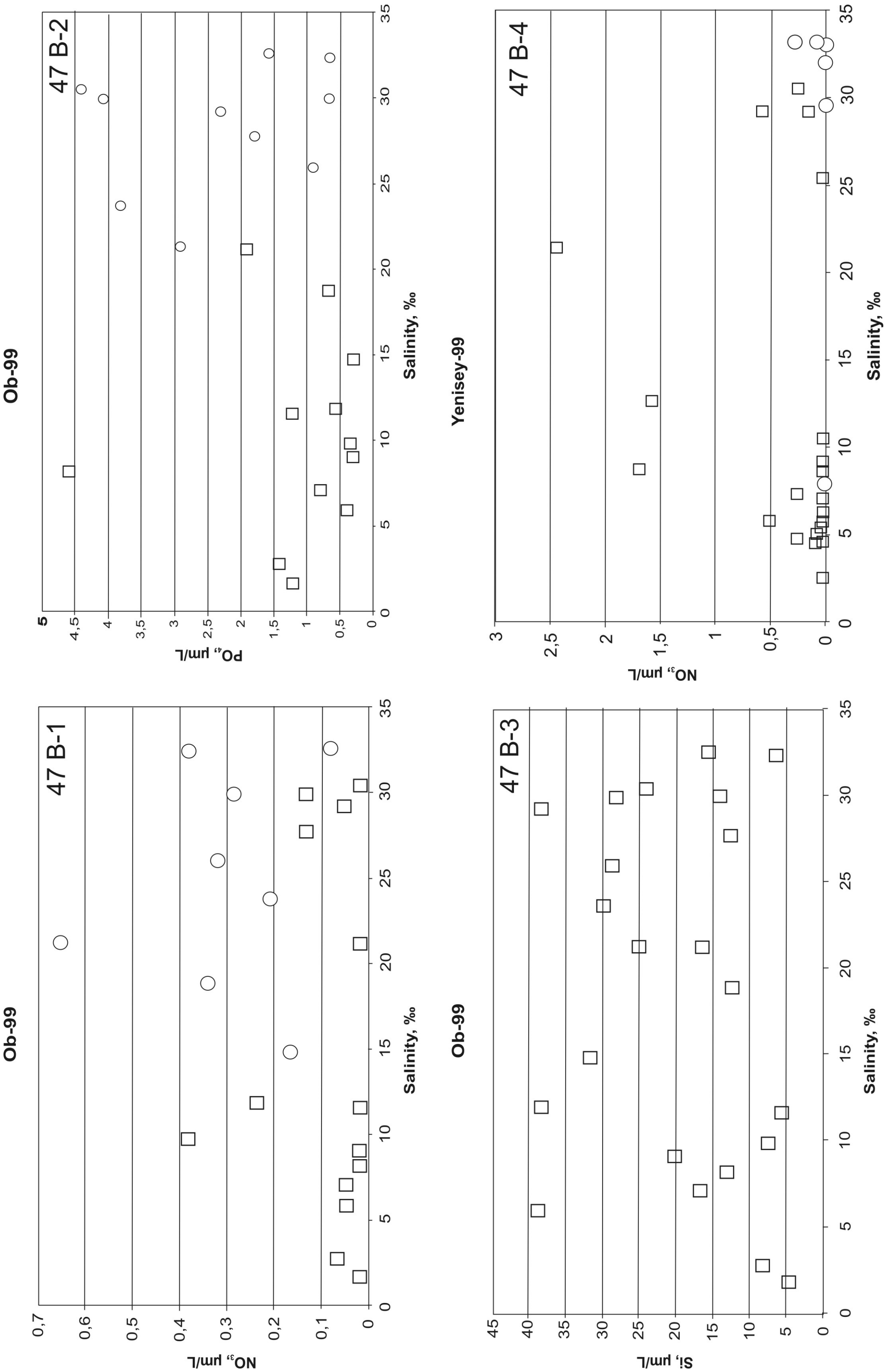

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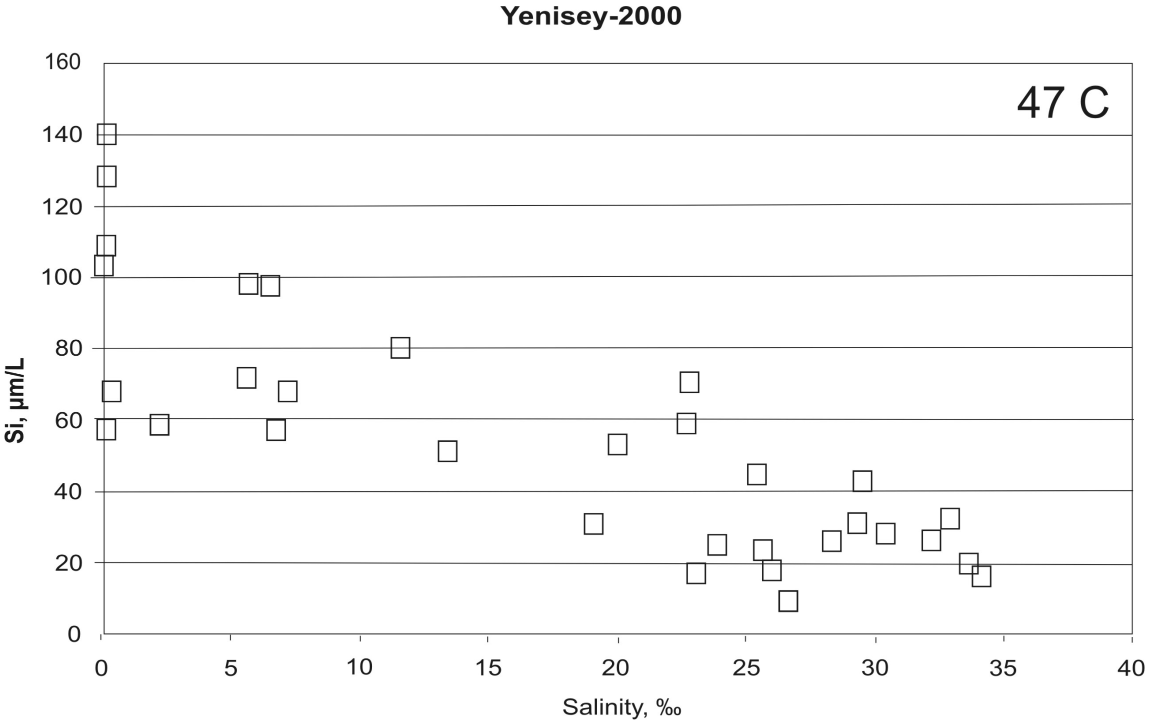


Figure 47 continued.

4.3.2.4 Trace elements

The studies on dissolved trace elements behaviour in the Ob and Yenisey Estuaries are very rare. Dai and Martin (1995) investigated the variations of Fe, Cu, Cd, Ni and Pb in dissolved and colloidal fractions. Savenko et al. (2001) studied the distribution of dissolved Sr, F and B in Ob and Yenisey Estuaries. Both works were carried out on materials of the 49-th cruise of the R/V "Dmitry Mendeleev" (1993). In other work (Beeskow and Rachold, 2003) dissolved Fe, Mn and Sr were measured in the Yenisey Bay.

F, B and Sr

The results of the field observations in the estuarine zones of the Ob and Yenisey (Savenko et al., 2001) have shown that the distribution of dissolved Sr, Ca, F and B was conservative and common in both estuaries (Fig.48 A). With increasing salinity Sr and Ca concentration is increasing linear, and can be described by the following equation:

$$[\mathrm{Sr, mg/l}]=0.14+3.84\times10^{-4}[\mathrm{Cl, mg/l}],\ r=0.995,\ n=22$$

$$[\mathrm{Ca, mg/l}]=19.4+0.0202[\mathrm{Cl, mg/l}],\ r=0.993,\ n=22$$

The Sr/Ca weight ratio in the transition from river to sea water increases slightly from 0.008-0.012 in the upper estuaries to 0.018-0.020 in the adjacent part of the Kara Sea.

Dependences of F and B on Cl were also common in both estuaries and had the linear form:

$$[\mathrm{F, mg/l}]=0.010+6.68\times10^{-5}[\mathrm{Cl, mg/l}],\ n=0.977,\ n=22$$

$$[\mathrm{B\ , mg/l}]=0.082+1.95\times10^{-4}[\mathrm{Cl, mg/l}],\ n=0.989,\ n=18$$

The ratios F/Cl and B/Cl were decreasing monotonously towards the sea up to (0.05-0.07) x10^{-3} and (0.18-0.22) x10^{-3} accordingly at chloride above 3.5 g/l.

The dependence of Sr, Ca, F and B on chloride (salinity) is also observed in other Russian Arctic rivers (North Dvina, Kem', Onega in the White Sea basin) (Savenko, 2003). Low concentrations of these elements in river discharge and close accordance of chemical composition of waters in the shelf marine aquatoria and in the World Ocean were typical for these rivers. The behaviour of these elements in the mixing zones is strictly conservative and with high correlation coefficients when described by common equations.

Fe

As it was demonstrated by Dai and Martin (1995) the so-called "dissolved" iron consists of 89-92% and 97% of colloidal fraction in Ob and Yenisey, respectively. Fe is strongly removed in both estuaries (Fig. 48 B). The overall conservativity of truly dissolved Fe indicates that the flocculation of colloidal material is responsible for the removal of "dissolved" Fe. The nature of this removed fraction of colloids is not clear (Dai and Martin, 1995). The results do not indicate whether this flocculated colloidal fraction is organic, inorganic or both. It is probably related to humic substances, macromolecules of which removed in estuaries.

Dissolved iron was determined in water samples of the Yenisey Estuary ("BP"-2000, this work), but the sensitivity of the direct ICP-OES method (lim det – 20 µm) prevents the measurement of the low iron concentrations in saline water. In all marine samples Fe concentrations were below detection limit. These results are in agreement with the conclusion of the non-conservative behaviour of Fe in the Ob and Yenisey Estuaries.

Pb

The concentration of "dissolved" Pb in the Ob River ranges 55-83pM (11-18 ng/l). In the Yenisey River its concentration is 2-3 times lower (25-29pM=5.2-6.1ng/l) (Dai and Martin, 1995). Colloidal fraction accounts for 42-52% of "dissolved" Pb in the Ob River and 22% in the Yenisey River. "Dissolved" Pb shows the same removal in both estuaries (Fig.48 C) but is less significantly than that of Fe, while truly dissolved Pb behaves conservative. The relatively significant removal of Fe and Pb in the Ob Estuary as compared to the Yenisey Estuary is probably related to the higher abundance of colloids in the Ob River.

Cu

Both, colloidal Cu and its proportion in the "dissolved" fraction are higher in the Ob Estuary than in the Yenisey Estuary.

The metal shows conservative behaviour in "dissolved" and colloidal fractions in both estuaries (Fig.48 B). This is due to the organic character of colloidal Cu, preventing its flocculation. Evidence for this mechanism is the correlation between colloidal Cu and organic colloidal carbon found in both estuaries (Dai and Martin, 1995).

Ni

The average concentration of "dissolved" Ni in river water is 1.3 µg/l and ≈0.5 µg/l in Ob and Yenisey respectively. Colloidal Ni comprises about 50% of dissolved Ni in the

Ob River and 60% in the Yenisey River. The distribution of dissolved Ni reveals a conservative behaviour in the Ob Estuary and non-conservative behaviour in the Yenisey Estuary (Fig.48 C). Although desorption of Ni from particles could cause some excess of dissolved Ni at salinity 0-10‰, it is more likely to consider this excess as a result of a biological regeneration process (excess dissolved Ni does not occur in the Ob Estuary because the biological activity was lower than in the Yenisey Estuary). In both estuaries a good correlation was found between colloidal Ni and colloidal organic C.

Cd

The "dissolved" Cd concentration ranges from 0.5 to0.9 ng/l and from 1.2 to1.8 ng/l in the Ob and Yenisey, respectively. These are the lowest values reported so far for major world rivers. However, in winter (December 2001) Cd concentration in the Ob River near Salekhard was higher with values between 1.8 and 12 ng/l (Table 10), near the world river average level of 10 ng/l. Colloidal Cd concentrations in the Ob River accounts 50-58% and in the Yenisey River 76% from dissolved Cd. The element has a complex distribution trend with salinity and a patchy occurrence in both estuaries (Fig. 48 B). The increase in concentration is probably related to desorption of particulate Cd. However, there is an alternative explanation, since a direct correlation between dissolved Cd and nutrients (nitrates, phosphates) occurs. It suggests that high Cd concentrations may be also associated to this nutrient regeneration (Dai and Martin, 1995).

Hg

The reliable concentration of dissolved mercury was determined in Ob, Yenisey and Lena Rivers and adjacent coastal sea water by Cossa et al. (1993), Couquery et al. (1995) and Cossa et al. (1996). The average concentration of dissolved Hg was 0.56±0.12(0.48-0.64)ng/l in the Ob River, 0.30±0.14(0.16-0.42)ng/l in the Yenisey River and 1.0±0.12(0.9-1.8)ng/l in the Lena River.

The data on the behaviour of dissolved Hg in Ob and Yenisey Estuaries show a simple mixing of river and sea water for salinity above 10‰, without any evidence of removal or addition of Hg. So, it's possible to say about quasi-conservativity (due to high scattering of data) of dissolved Hg in both estuaries.

Ba

Behaviour of dissolved Ba in the mixing zones of the Arctic rivers, including the Ob, Yenisey and Lena, was studied by Guay and Falkner (1998). Water samples were collected in August-September of 1993, 1994 and 1995 (in 1993 on board of R/V “Dmitry Mendeleev”). The results are shown in Fig.48 C. In 1993 Ba increased from 60-70 nM in the Ob River at near-zero salinity to maximum of 91nM at salinity about 5%o. Past the maxima at low salinity Ba decreased seaward. In 1994, dissolved Ba sharply decreased from 102 nM to 37 nM as salinity increased from 0 to 1‰ within 100 miles downstream. The maximum value of 138 nM was detected at 9.4‰. At salinity >20‰ concentration decreased again.

In the Yenisey River the similar situation was found. In 1993 and 1995 the maximum values of 175 nM and 115 nM, respectively were measured at salinity of 5‰. In 1994, the sharp decrease was detected in a salinity range 0-1‰. Upstream Ba concentration of 102 nM decreases to 24 nM at station near the river mouth. At salinity of 19.2‰ the highest concentration 86 nM occurred. At salinity above 20‰ the concentration of Ba decreased.

In both estuaries many of the points at intermediate salinity lie below conservative mixing lines. The authors (Guay and Folkner, 1998) consider that the non-conservative behaviour of Ba is due to the biological activity in the estuaries. The Ba concentration in the Mackenzie River (138-574 nM) is much higher than those measured in any Eurasian Arctic river (12-175nM). The high Ba load of the Mackenzie River implies the existence of Ba-rich rocks in its catchment area such as the economic deposits of barite in regions of British Columbia and the Yukon Territory.

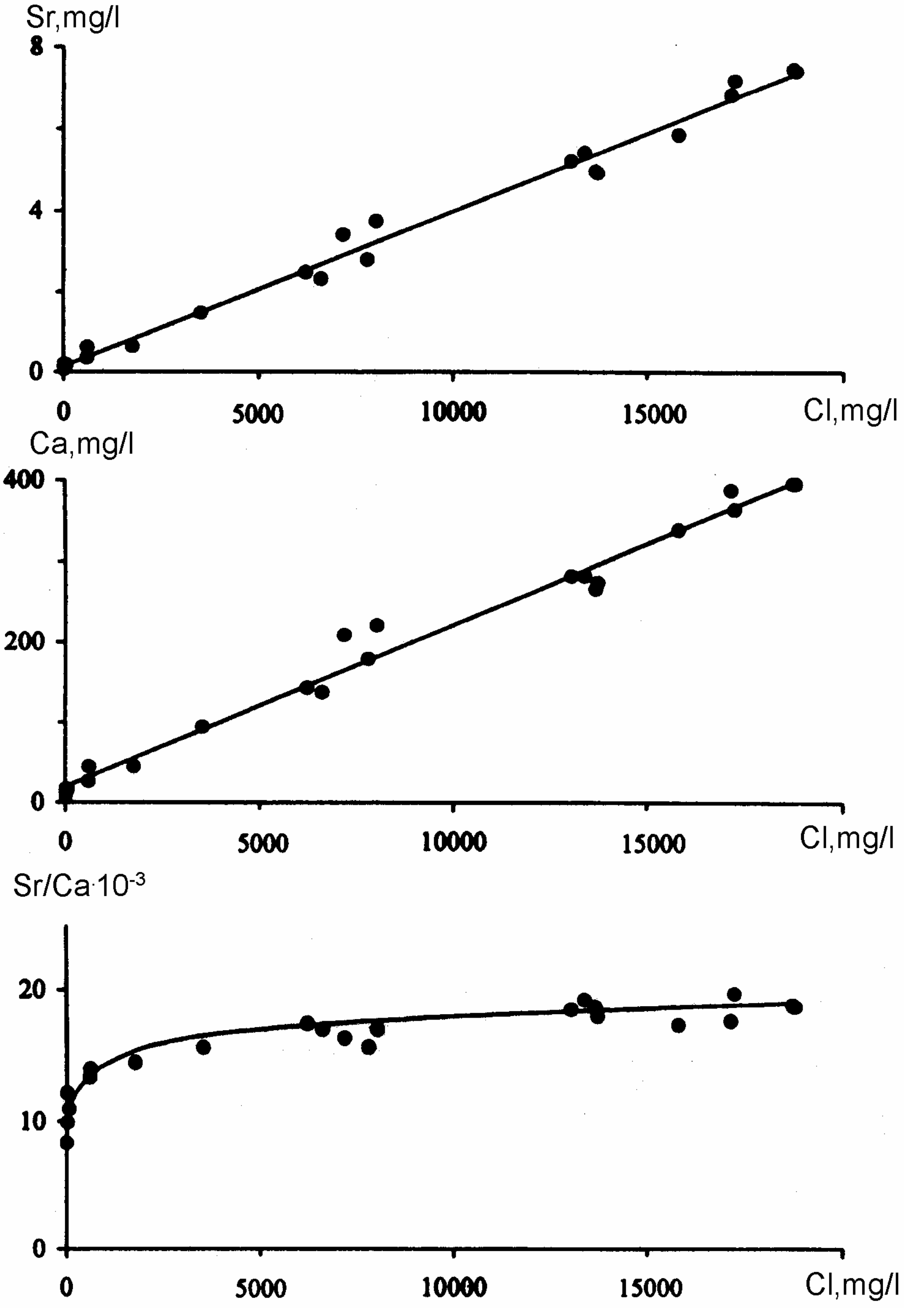


Figure 48A1 Distribution of dissolved trace elements against salinity in the Ob and Yenisey Estuaries: Sr, Ca and Sr/Ca (Savenko, 2004);

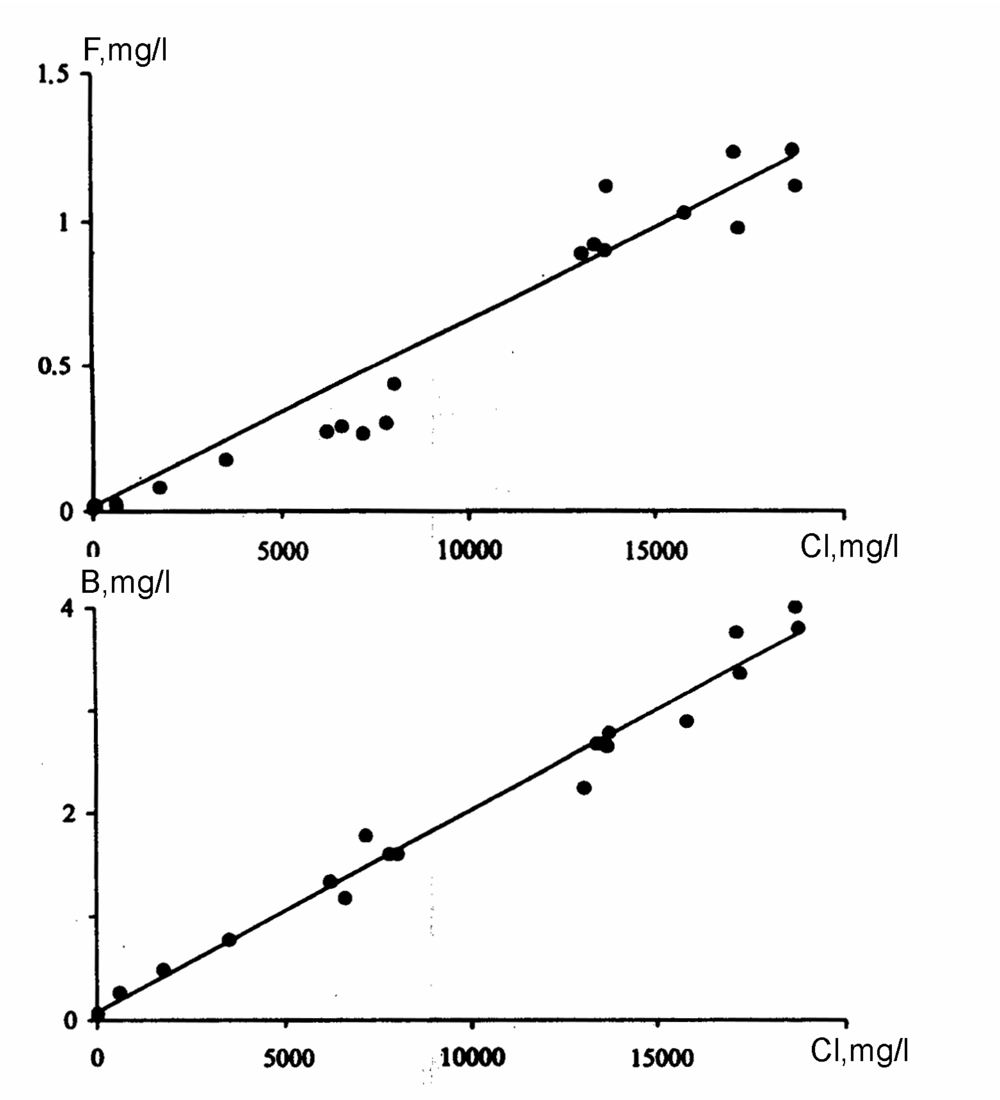


Figure 48A2 Distribution of dissolved trace elements against salinity in the Ob and Yenisey Estuaries: F and B (Savenko, 2004);

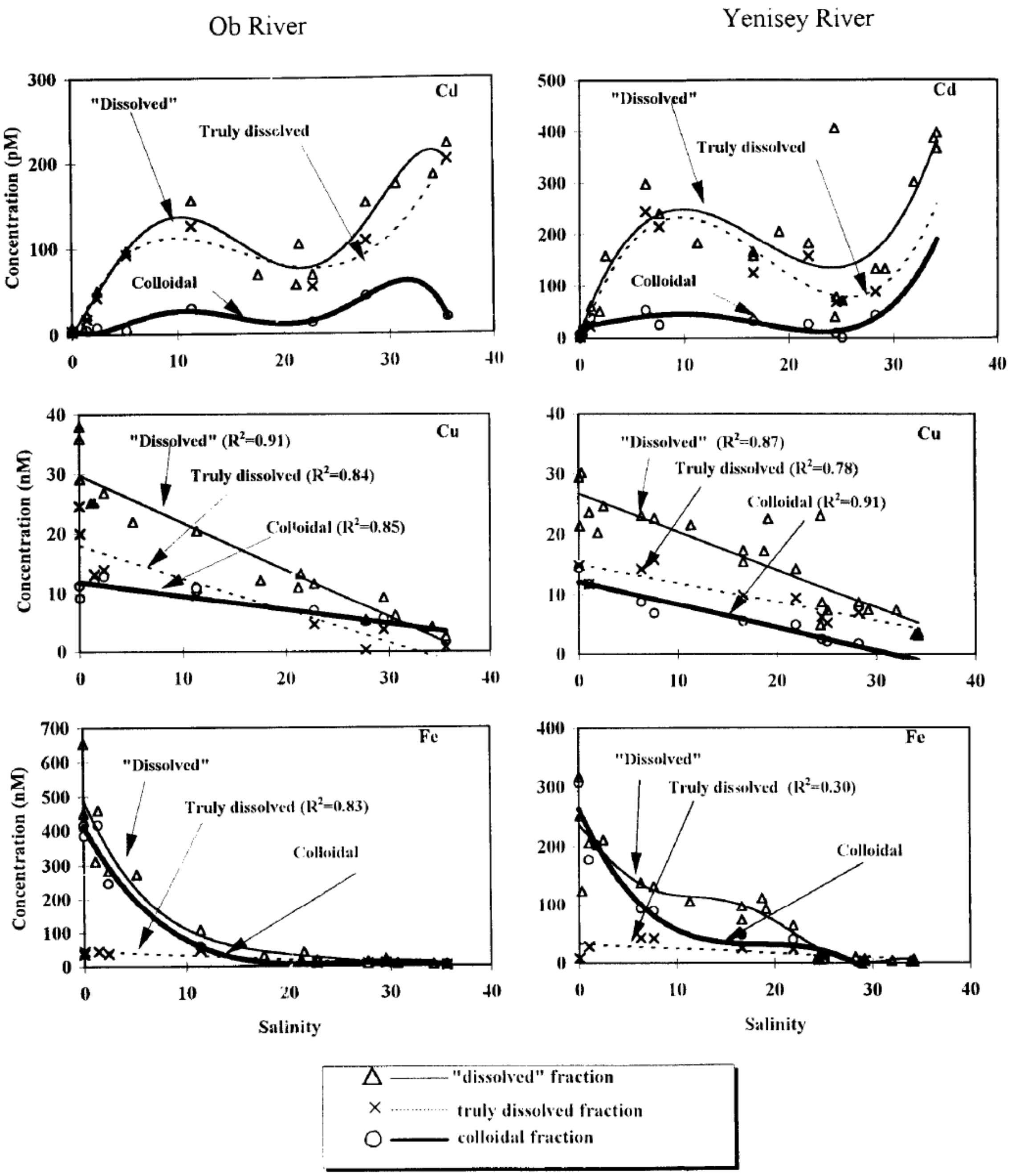


Figure 48B1 Distribution of dissolved trace elements against salinity in the Ob and Yenisey Estuaries: Fe, Cu and Cd in "dissolved" fraction, truly dissolved fraction and colloidal fraction (Dai and Martin, 1995);

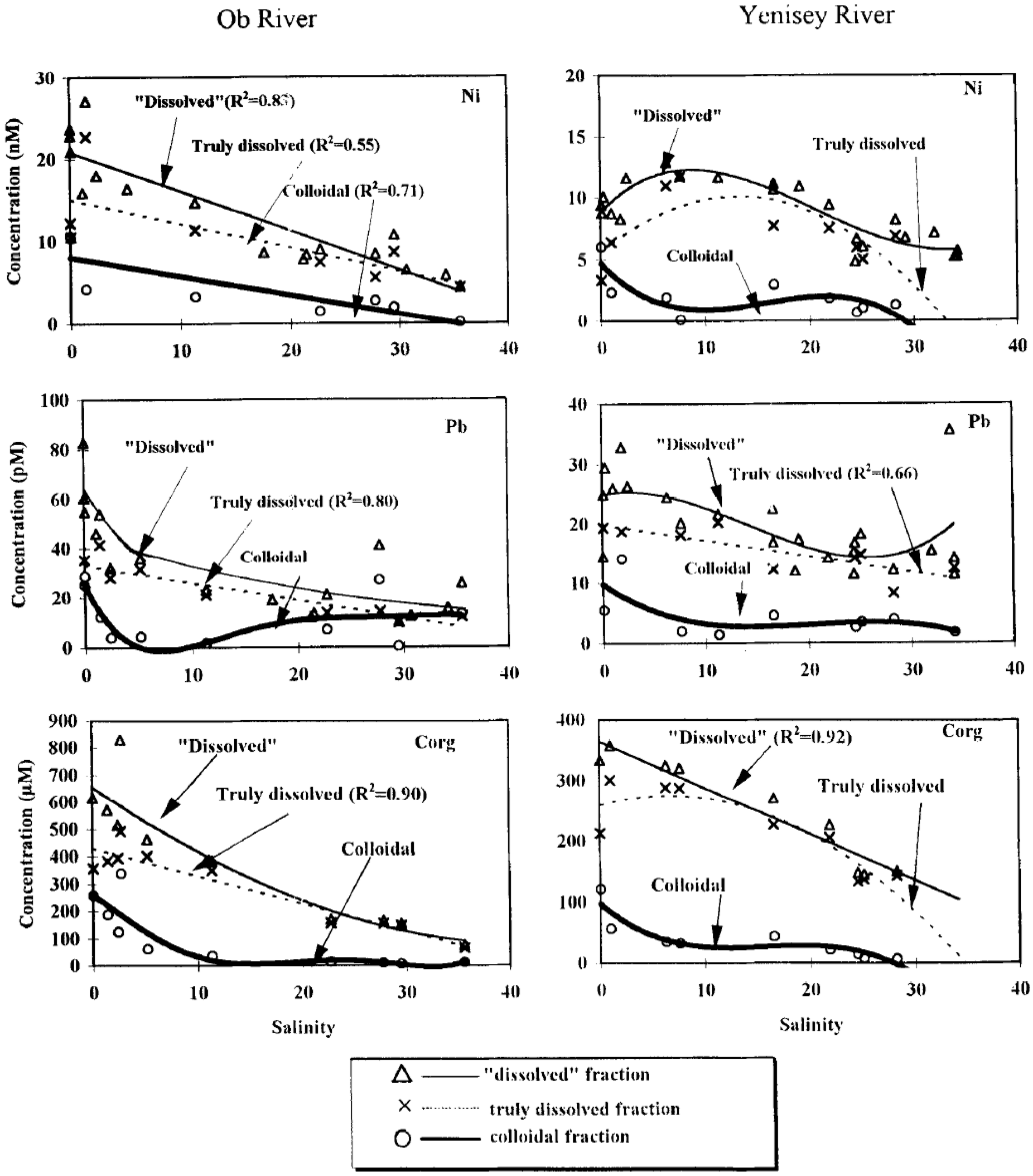


Figure 48B2 Distribution of dissolved trace elements against salinity in the Ob and Yenisey Estuaries: Ni, Pb and DOC in "dissolved" fraction, truly dissolved fraction and colloidal fraction (Dai and Martin, 1995);

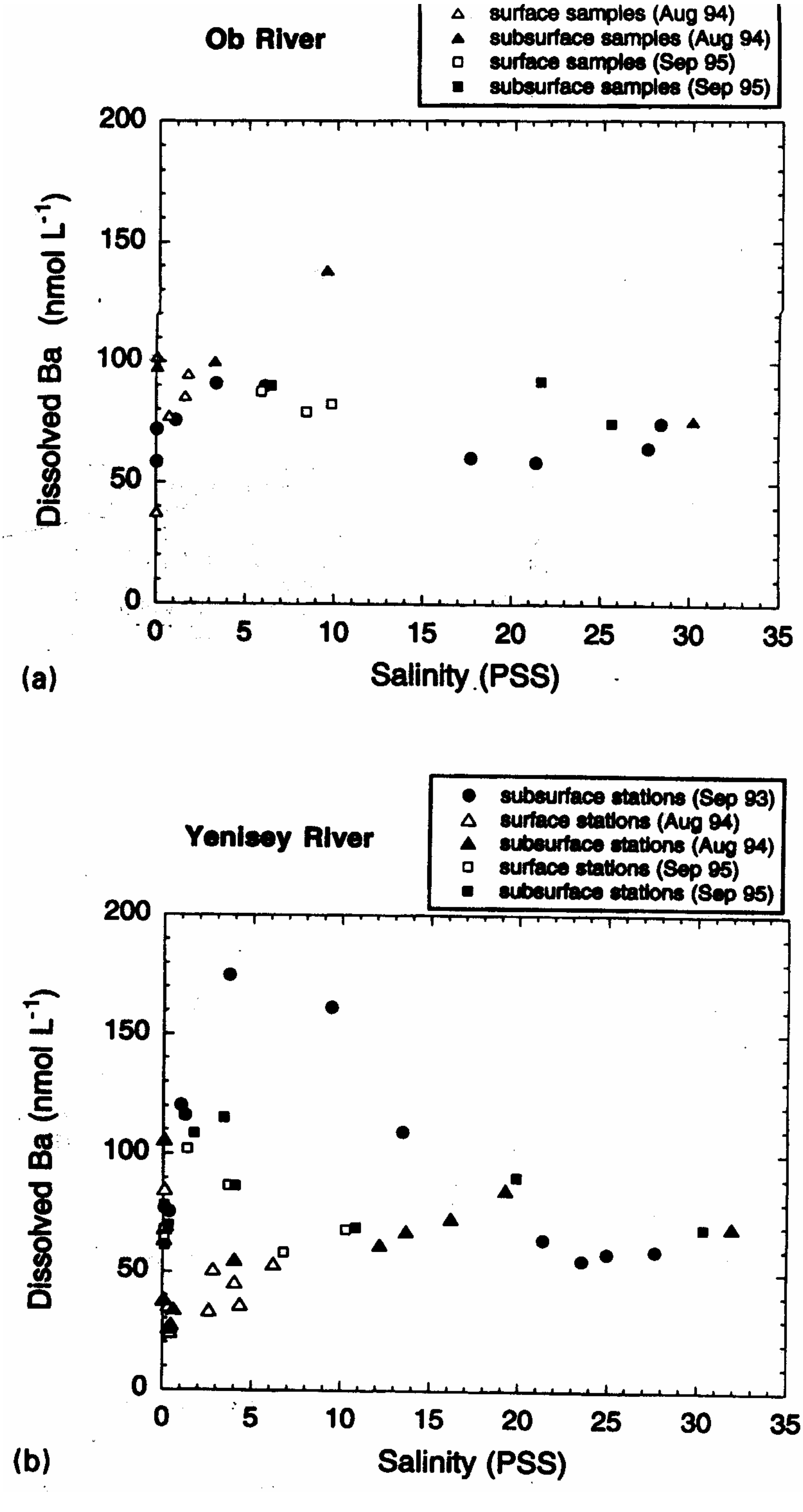


Figure 48C Distribution of dissolved trace elements against salinity in the Ob and Yenisey Estuaries: Ba: Ob River Estuary in 1993-1995; Ba: Yenisey River Estuary in 1993-1995 (Guay and Falkner, 1998).

4.3.3 Primary production (PP)

Until the 90-th years of the last century the data on PP in the Siberian estuaries and seas were practically absent. The first quantitative determinations of PP in the water column of the Ob and Yenisey Estuaries accompanied the determinations of chlorophyll a and underwater irradiation at several depths of the euphotic zone were carried out in the 49-th cruise of the R/V "Dmitry Mendeleev" at the end of period of seasonal succession of plankton in 1993 (Vedernikov et al., 1994).

The results of chlorophyll a concentrations and the PP values along the sections through the Ob and Yenisey Estuaries are presented in Fig.49. On the river stations 4417 and 4418 in the Ob Guba high and homogenous with depth chlorophyll a concentrations were measured (4-6 mg/m^3). In the photosynthesis zone (2-6 m layer due to low transparency of waters – 0.2-0.5 m) 15-25% of total chlorophyll a in a water column only were concentrated. On the northernmost stations 4395 and 4397 with salinity >17‰ and surface water temperature <2°C the chlorophyll A concentrations in the photosynthesis zone and in the whole water column were low.

In the Yenisey Bay the highest chlorophyll a concentrations were also found on the southernmost river stations 4408 and 4410. An increase of salinity and decrease of temperature from south to north was accompanied with decreasing chlorophyll a concentrations in the photosynthesis layer (which thickness expanded from 13-14 m on the southern stations to 25-35 m on the northern stations) and in the whole water column. Sharp gradients were observed at stations 4410 and 4413, the first frontal zone, where intensive mixing of river waters and brackish estuarine waters occurred. Significant variability of C_{fe} (PP value in a water column) along the transect may be explained by sharp changes of the values of the falling radiation (46-103 Cal/cm^2).

PP in the water column of the Ob Guba were in the range from 25 to 63 mgC/m^2·day while in the Yenisey Bay they appeared to be much higher with 107 to 312 mgC/m^2·day. Low PP values in the Ob Guba are explained not only by the low water transparency but also by unfavourable meteorological conditions for photosynthesis. The calculations (Vedernikov et al., 1994) show that at sunny days PP would increase by 2.4 times up to 90-160 mgC/m^2·day. Another reason of discrepancy of the C_{fc} values measured to high chlorophyll a concentrations was the low assimilation activity of phytoplankton. Assimilation number (AN) for the water column in the Ob Estuary ranged from 0.2 to 1.1 mgC/mg chlorophyll a in hour, while in the Yenisey Bay it was 1.1-2.1 mgC/mg chlorophyll a in hour. The narrow range of AN indicates that in the Yenisey Bay PP was to a higher extend depended on the quantity of phytoplankton than on its assimilation activity. On a base of these determinations Vedernikov et al.(1994) conclude that in the Ob Guba the limiting factors for PP were low water transparency, unfavourable weather conditions, and low physiological activity of phytoplankton. Low C_{fc} and AN in the Ob Estuary at high content of nutrients reveal the absence of their deficit.

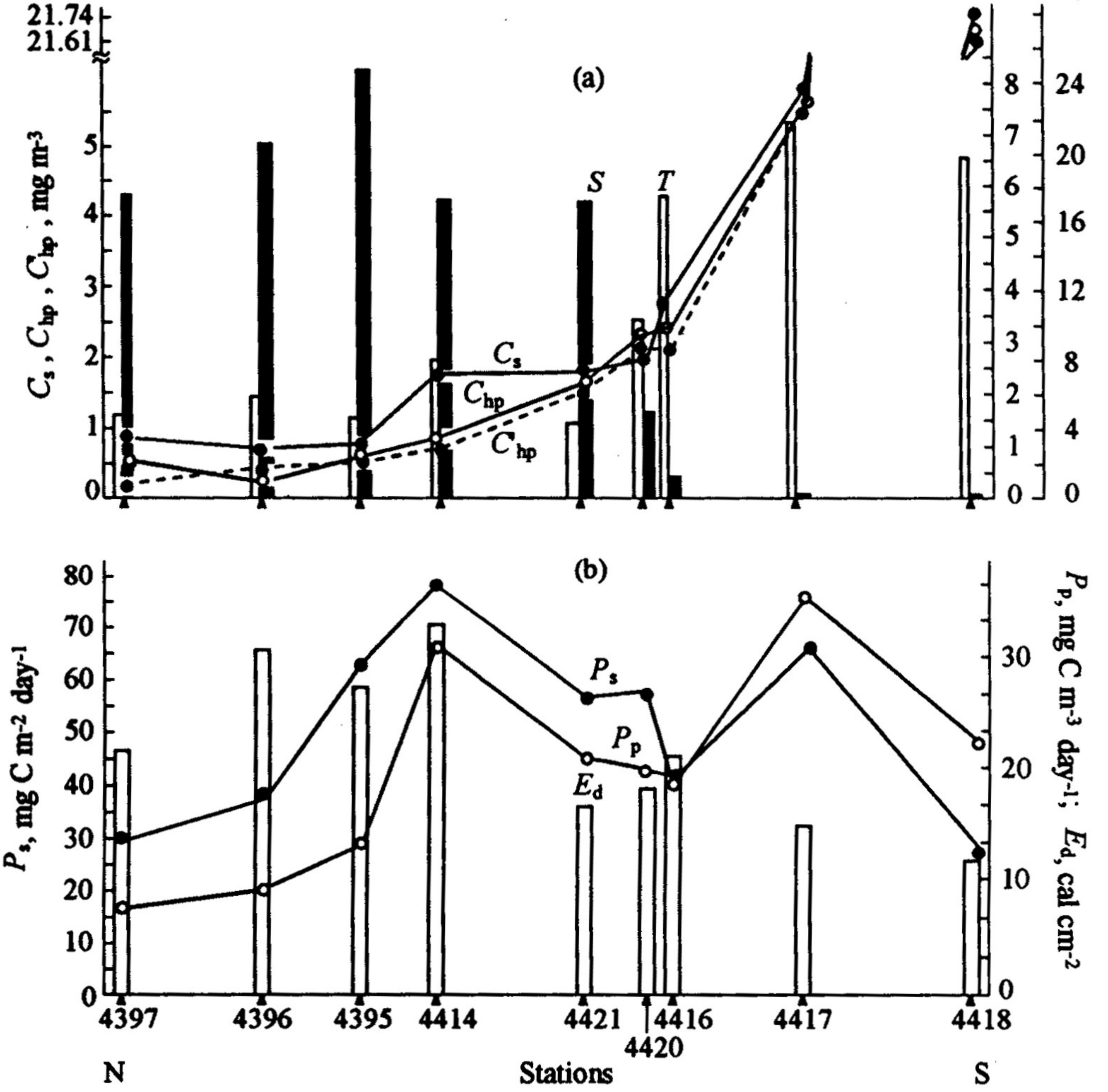


Figure 49A Distribution of chlorophyll "a" and primary production in the Ob sections: Cs, C_{ph} C'_{ph} – concentration of chlorophyll in the photosynthesis layer and in the water column, respectively; T and S – temperature and salinity in the surface layer; P_s and P_p – primary production in the surface layer and in the water column, and Ed – total downward radiation over the period of flasks exposure (half of a light day) (Vedernikov et al., 1994).

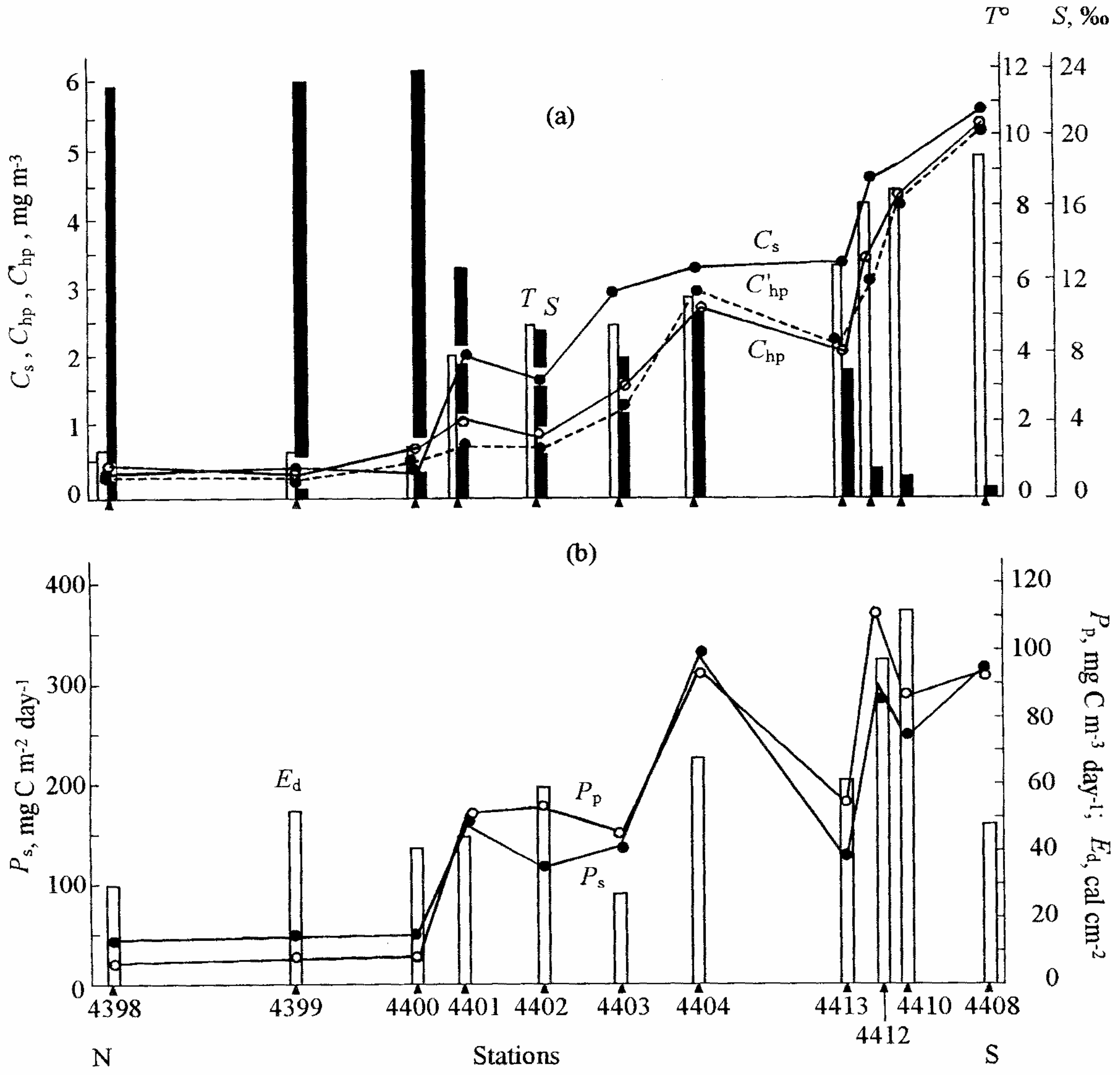


Figure 49B **Distribution of chlorophyll "a" and primary production in the Yenisey sections: Cs, C_{ph} C'_{ph} – concentration of chlorophyll in the photosynthesis layer and in the water column, respectively; T and S – temperature and salinity in the surface layer; P_s and P_p – primary production in the surface layer and in the water column, and Ed – total downward radiation over the period of flasks exposure (half of a light day) (Vedernikov et al., 1994).**

The low water transparency was also the main reason for relatively low PP in the Yenisey Bay with high chlorophyll a concentration. At the same time the low $Si_{diss.}$concentration (<10μm) in surface waters on stations with high salinity (>22‰) indicates that silica might be a limiting factor for PP. In the open Kara Sea low nutrient concentrations and low water temperature (<5°C) were the limiting factor for PP.

Chlorophyll a concentrations and the biomass of phytoplankton were measured in the expeditions of the R/V "Academic Boris Petrov" in 1997, 1999, 2000 and 2001. The results will be considered in details in Section 5.7.2.

4.3.4 Element behaviour in SPM

4.3.4.1 Concentration of SPM and its grain-size distribution

The average multi-annual SPM concentrations are 37 mg/l, 8 mg/l and 39 mg/l in the Ob, Yenisey and Lena (See Section 4.1). The SPM distributions along the Ob and Yenisey mixing zone are shown for September of 1993 (Shevchenko et al., 1997) and for September of 1997 (Lukashin et al., 1999) (Fig. 50 A-D). Both pictures show a general tendency of decrease in transit from river to sea, and three-layer structure with depth. High SPM concentrations are typical in river water and brackish waters with low salinity, in fresh surface water and near bottom saline waters where stirring of bottom sediments occurs. This structure was evident in 1993 and to also to a smaller extend in 1997.

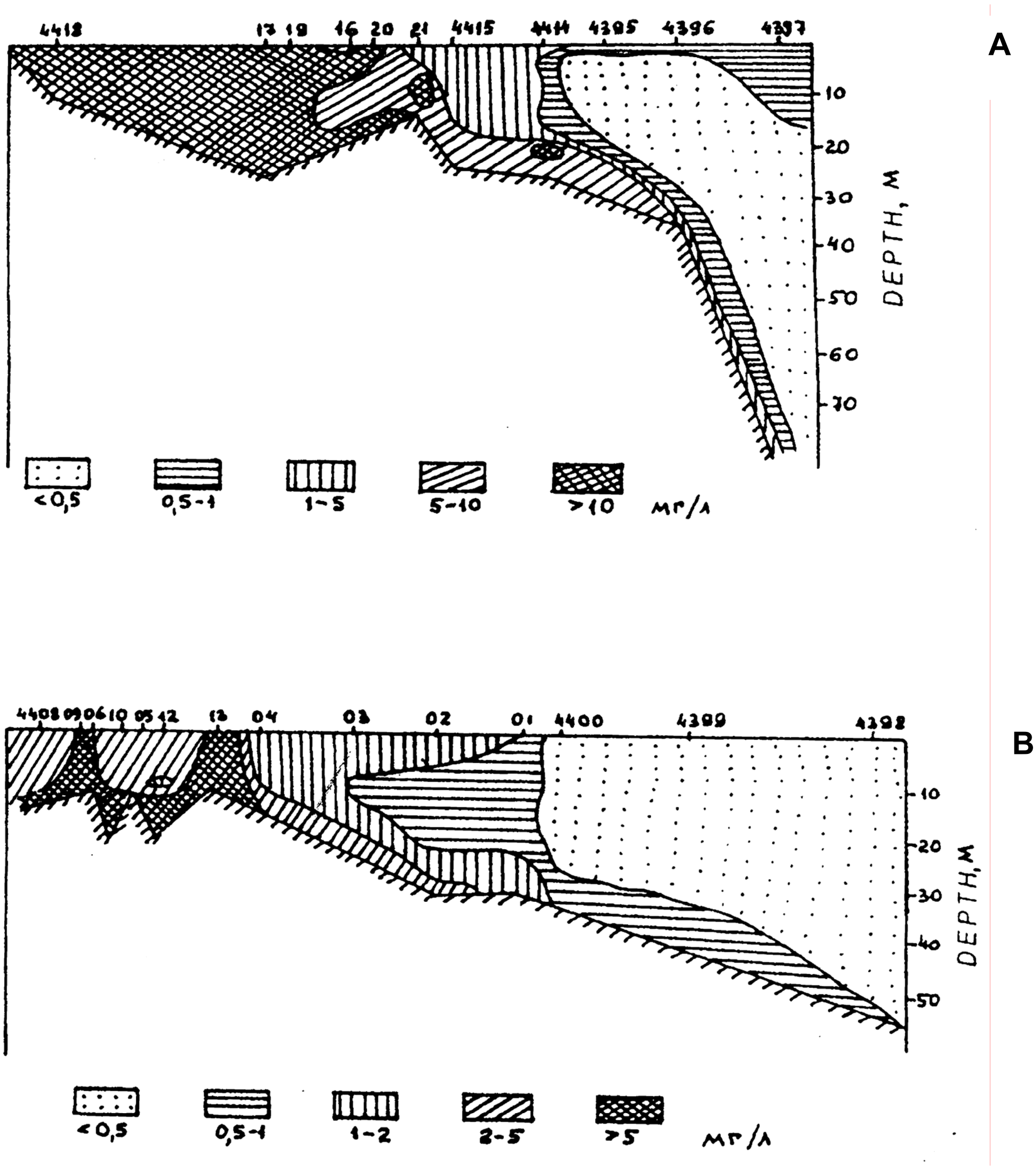


Figure 50A,B Distribution of SPM (mg/l) on transects in the Ob and Yenisey Estuaries in 1993 (Shevchenko et al., 1997).

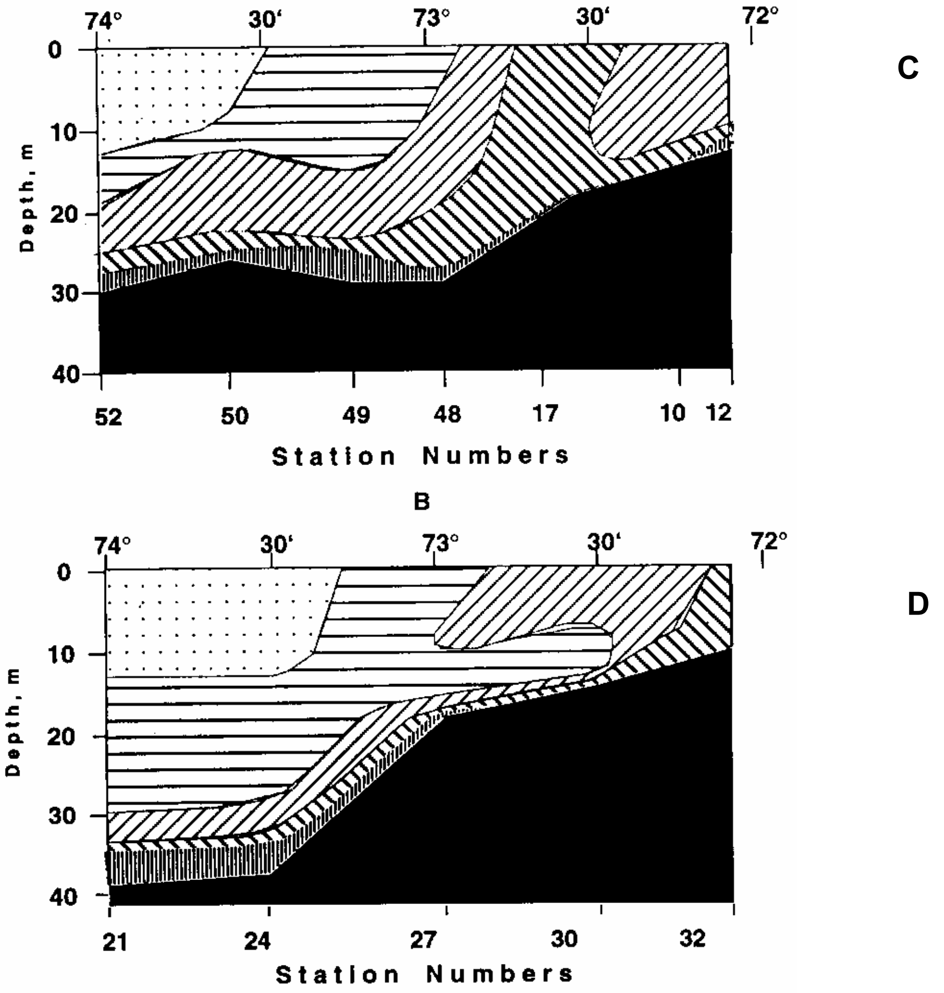


Figure 50C,D Distribution of SPM (mg/l) on transects in the Ob and Yenisey Estuaries in 1997 (Lukashin et al., 1999).

Similar dependencies are typical for the majority of large World rivers. This conform the conclusion that the main part of river SPM deposits in the estuarine mixing zone and does not penetrate into the open sea (Gordeev, 1983; Lisitzin, 1994, 1998)

The elutriation method was used to study the SPM grain-size distribution at the marine margins of Ob and Yenisey Rivers. The distribution of grain-size fractions in SPM in the Ob and Yenisey Estuaries at low salinity and at higher salinity (in a range 9-28‰) were found to be similar (Figs.7 and 30). This is unexpected because the effect of mechanical fractionation of SPM with salinity is well known (the finer SPM at higher salinity due to predominant sedimentation of coarse particles - see Section 4.3.1). The reasons of this similarity are different in two estuaries. The SPM samples of highest salinity from the Ob transect were obtained when the ship's track was deviated from south-northern to western direction (Fig.7). In the western part of the Kara Sea a circulation pattern is dominated by cyclonic gyre. The Novo-Zemelskoe current doubles at the Novaya Zemlya coast and directs towards south, the Yamal current doubles at the Yamal Peninsula and flows to the north. The velocity of both currents is in average of 10cm/s. The powerful Yamal current takes huge masses of shore and bottom SPM in the south-western part of the sea and transports them in northern direction. In the samples 30+31 (=O1), a significant, if not predominant, part of material of non-river genesis appeared.

The content of POC in these samples (3.8-4.3%) does not agree with POC content in the samples of similar salinity (10-23‰) (for example, in the sample 16 of the Yenisey transect with salinity > 12‰ POC=12.5%). These samples have a higher content of quartz (> 50%) and lower content of feldspars comparing to the river SPM. It means that quartz/feldspars ratio in sample O2 is two times higher than in sample O1. The bottom sediments of the SW part of the Kara Sea are characterized with high quartz/feldspars ratios (Levitan et. al., 1996; Gorbunova, 1996). Thus the sample O2 does not characterize in sufficient degree the marine end member of the Ob transect.

There is another reason of the grain-size distribution similarity of the river and marine samples in the Yenisey transect. The POC content in marine sample Y2 is three times higher than in river sample Y1. The set of minerals in both samples is very similar but sample Y2 contains amorphous silica (X-ray spectroscopy analysis) that is related to diatom bloom (data of the biologists-participants of the cruise). The size of the diatom shell is about 0.02-0.2 mm (Lisitzin, 1978) and explains the coarser than expected grain-size composition of sample Y2. We cannot exclude also a possibility of crushing of the coarser particles of SPM (in off-shore area mainly of biogenic origin) during sampling. On the other hand, there is evidence that fine particles agglomerate during centrifugation to form coarse particles.

Fig. 30 shows the distribution of the bottom sediment grain-size fractions in four stations of two transects. The picture is typical for clayey muds (by Bezrukov/Lisitzin classification): the main maximum characterizes the pelitic fractions (< 0.01 mm) and subordinate maximum is related to the fraction of coarse aleurit-fine sand (>0.05 mm).

4.3.4.2 Major elements

In the estuaries with low biological productivity the behaviour of major elements in SPM (presented as ratio (Me/Al)est./(Me/Al)riv.) does not change with salinity. This ratio is about 1 for example in the estuaries of the Congo River and the Tay River (Scotland) (Sholkovitz, 1979; Sholkovitz et al., 1978). In the Amazon Estuary, where PP is high, the ratios Si/Al, Ca/Al, Mg/Al, Ti/Al, P/Al are sharply increased at salinity > 10‰.

In the biological step of the Amazon marginal filter the SPM concentration drops below 2-3 mg/l (in river water 300-500 mg/l) and due to phytoplankton bloom the terrigenous component of SPM is about 5% only. The main part of suspension is of organic origin. An active assimilation of major elements is the main reason of their high metal/Al ratios.

In the Arctic estuaries the PP is low and the ratios of major elements to Al are quite stable. The examples of variations of Fe/Al, Si/Al, Ca/Al, Ti/Al and P/Al in SPM of the Ob and Yenisey Estuaries related to the same ratio in average fluvial SPM are shown in Fig. 51 A and B. Another example is shown in Fig. 51 C on the results of the expedition "DM" in 1993. Here, separated SPM samples were used. In the most cases the ratios (not related to the ratio Me/Al in river SPM) change very slightly with salinity and in river water slightly lower ratios for Mg, K and Na, and higher for Ca, Fe and Mn were observed.

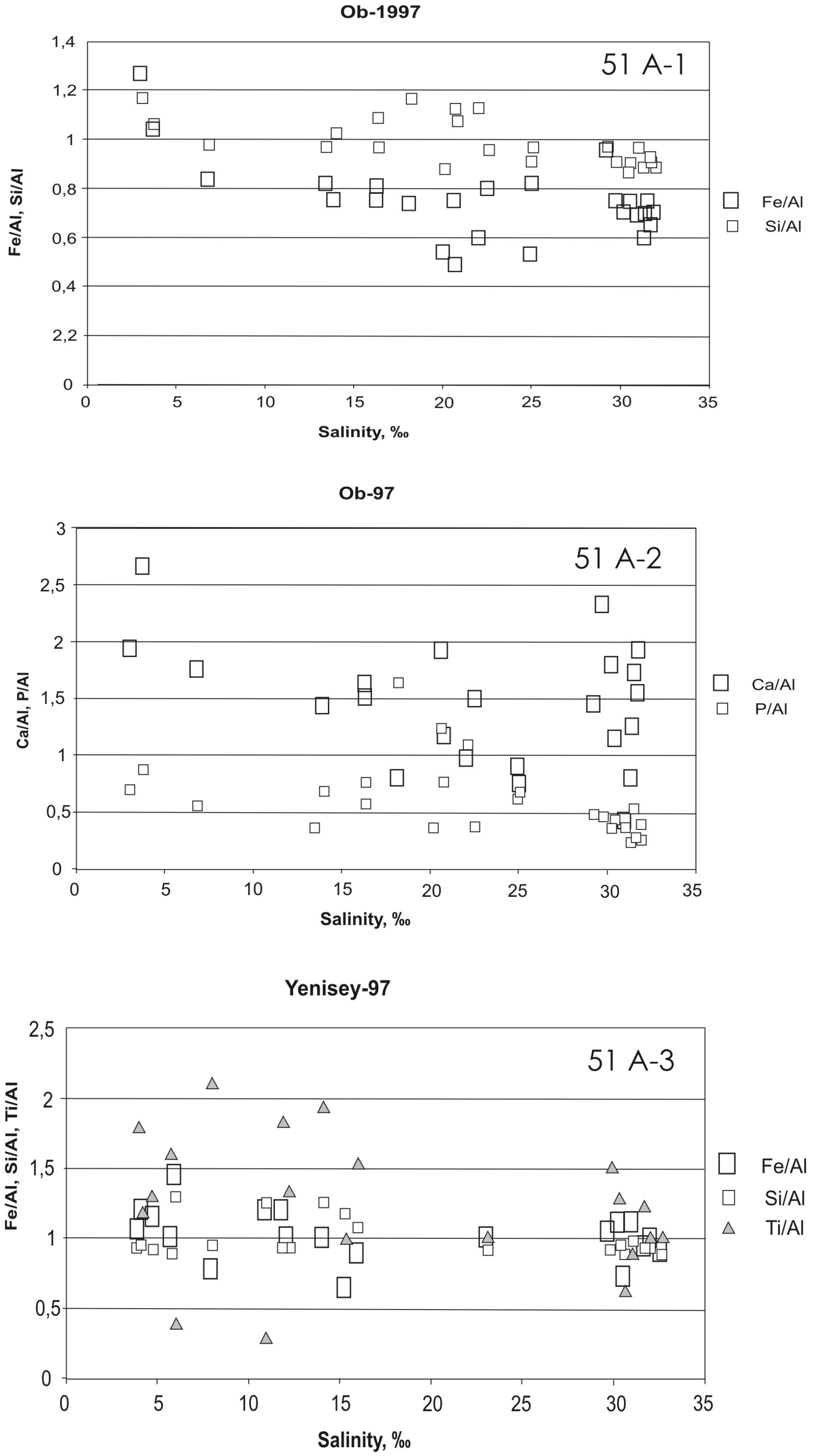
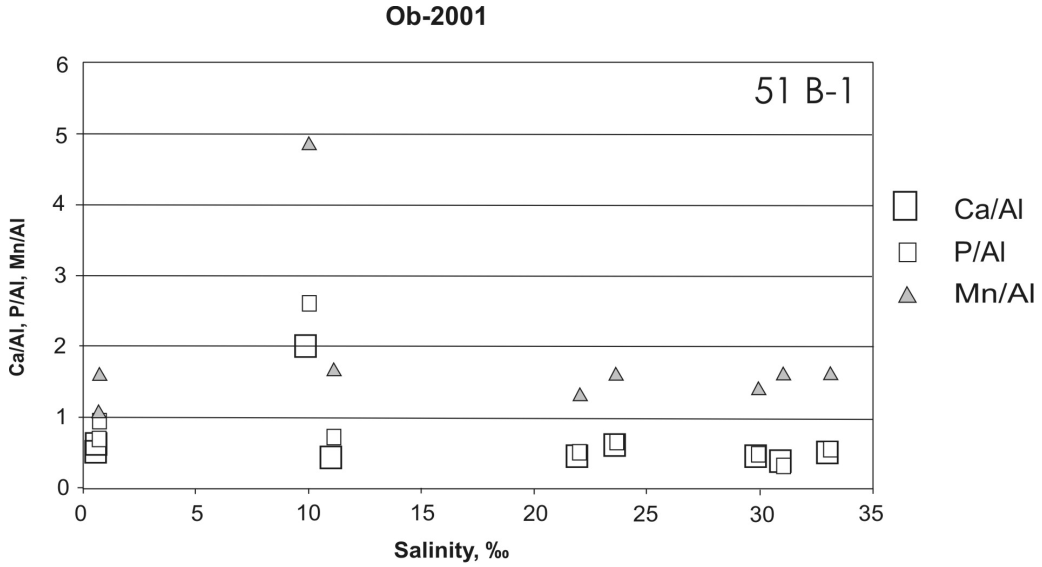
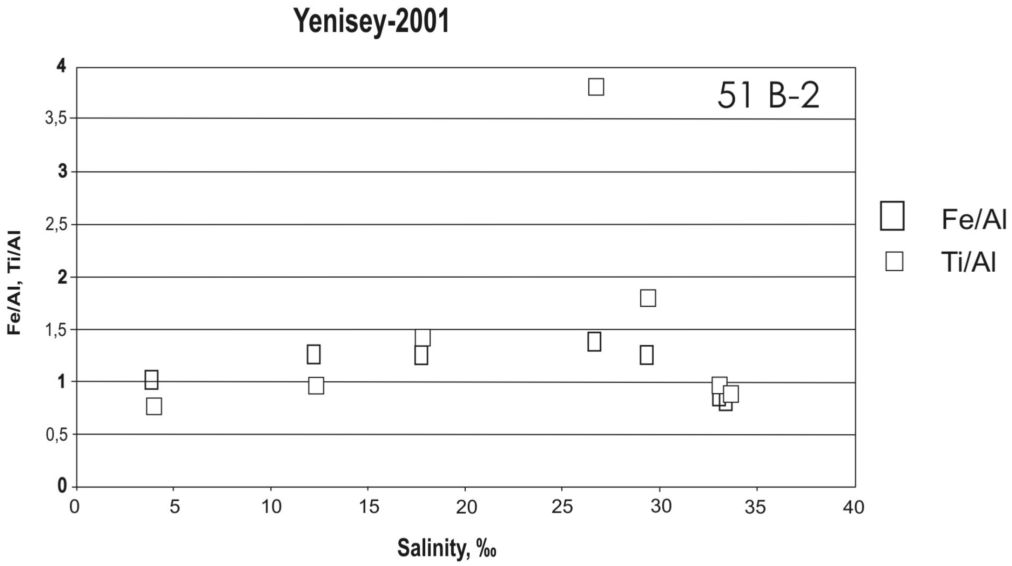


**Figure 51 Variations of the ratios of major elements to Al (Me/Al) in SPM of the Ob and Yenisey Rivers to the same ratios in SPM of the estuaries:
A. 1997: Ob – Si, Fe (A-1) and Ca, P (A-2), Yenisey – Fe, Si, Ti (A-3) (Lukashin et al., 1999); B. 2001: Ob – Ca, P, Mn (B-1), Yenisey – Fe, Ti (B-2) and Ca, P (B-3) (Rachold, unpublished data); C. 1993: The ratios Na/Al (C-1) and Ca/Al (C-2) in SPM and bottom sediments.**





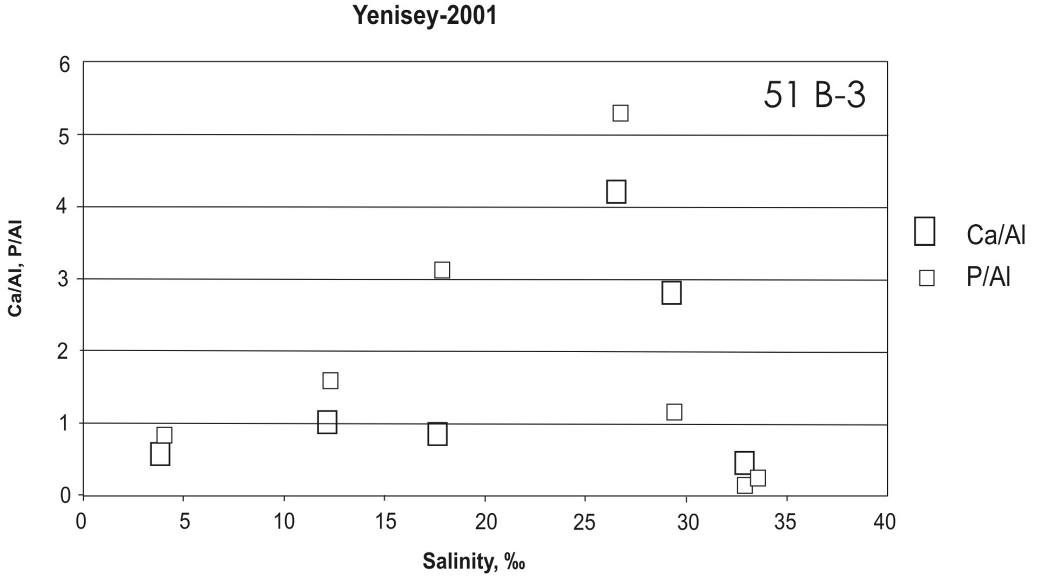


Figure 51 continued.

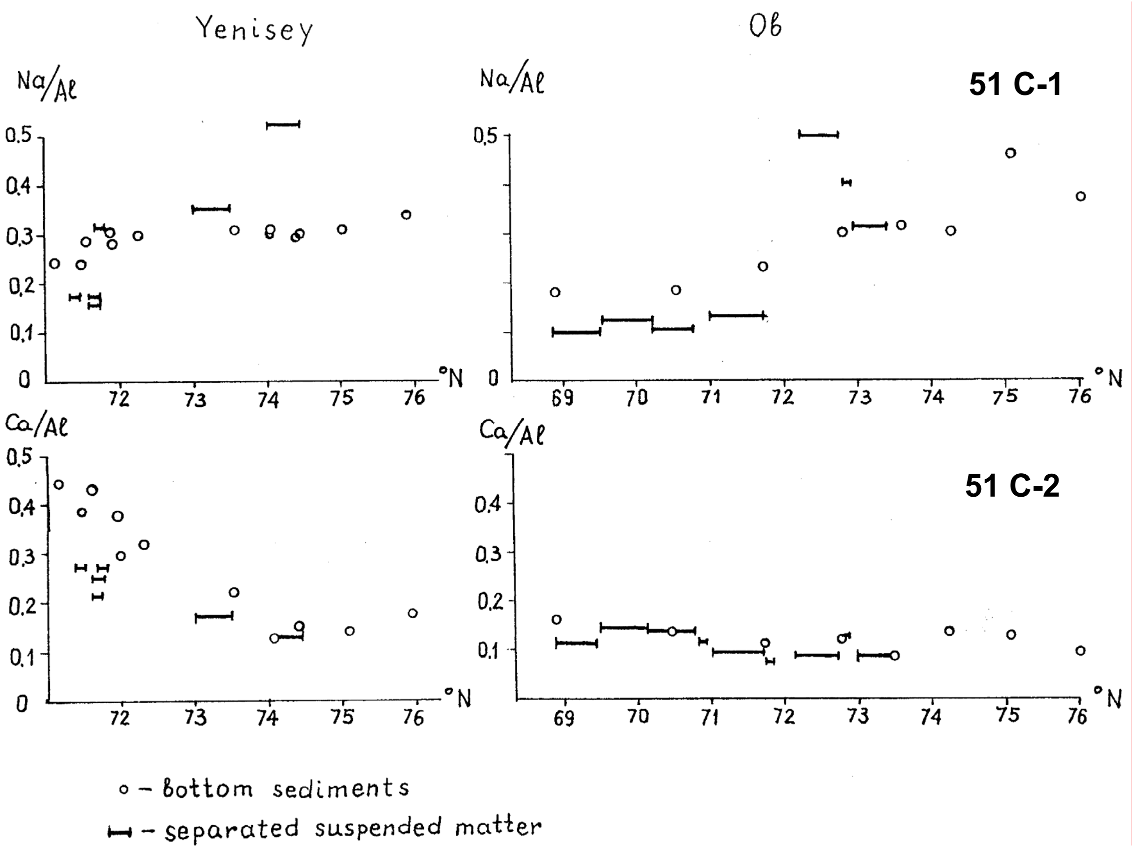


Figure 51 **continued**

A similar picture was observed by Beeskow and Rachold (2003) for the Yenisey Estuary. They consider that Mg, K and Na, which are the main dissolved cations in seawater, are replaced and enter the dissolved fraction with increasing salinity. For Ca the situation is opposite because this element is the main cation in river water.

4.3.4.3 POC

The distribution of POC in the mixing zones is related to the distribution of DOC. In Section 4.3.2.2, the conservative behaviour of DOC in the Ob and Yenisey Estuaries was shown (the results of BP-97, BP-99, BP-00, DM-93 and other). It is expected also that and POC distribution (in μMC) would be conservative or quasi-conservative.

A mixing experiment of Yenisey water (S=0) and open Kara Sea deep water (S>33‰) indicates a quasi-conservative behaviour of POC with, relative to the theoretical conservative mixing line, very little DOC loss in the low salinity range (<20 μMC or about 3%) (Kohler et al., 2003) (Fig.46). A small increase of POC concentrations in the same salinity range coincided with this decrease of DOC. But this small loss (3%) of DOC is in the analytical range of accuracy of the analytical methods.

The factual distribution of POC (μMC) in both estuaries conform these expectations although the scattering of points near the mixing line is relatively large (Fig.52 A). More interesting is the percental distribution of POC in dry SPM weight. This approach allows to determine the salinity ranges where SPM is enriched in organic carbon and to compare it with distribution of other chemical elements.

The distribution of POC (%) versus salinity in the Yenisey and Ob Estuaries is shown in Fig.52 B-F. More or less stable content of C_{org} (5-8%) was supported in the Yenisey Estuary (BP-2000) at salinity 0-10‰. Seawards, the SPM becomes enriched in C_{org} by up to 15-20% in salinity range from 15 to 25‰. Few samples only with salinity near 30‰ again contain the same 5-7% C in SPM.

At low salinity (<10‰) the SPM concentration is high and prevents the penetration of sun light into the water column. Despite of significant nutrient concentrations, phytoplankton is unable to growth actively (the first two steps of the MF). When the water becomes cleaner the phytoplankton bloom enriches the surface SPM in organic carbon up to 15-20% C_{org}.

Note, only SPM samples with salinity 25-33‰ from near bottom water were available. This SPM is a mixture of deposited from the water column particles, which may loose organic carbon, with the particles from the bottom sediments with low content of C_{org}. So, in arctic estuaries it is not possible to collect surface water samples with salinity close to that of open ocean water. In the opposite situation high POC (%) at salinity 30-34‰ would be expected, instead of observed 5-8% C_{org}..

A very similar picture was observed in the Yenisey Estuary in 1997 (BP-97). POC content in the salinity range 0-10‰ and 30-34‰ is low. At intermediate salinities (10-20‰) POC values increase significantly. POC distribution in the Ob Estuary (BP-97) is characterized by higher range of salinity (up to 15‰) in the first stage of distribution with low and stable POC (%). This might be explained by the higher SPM concentration in the Ob River and Estuary compared to the Yenisey. This pattern of POC distribution in the estuaries may influence the behaviour of some chemical elements in SPM.

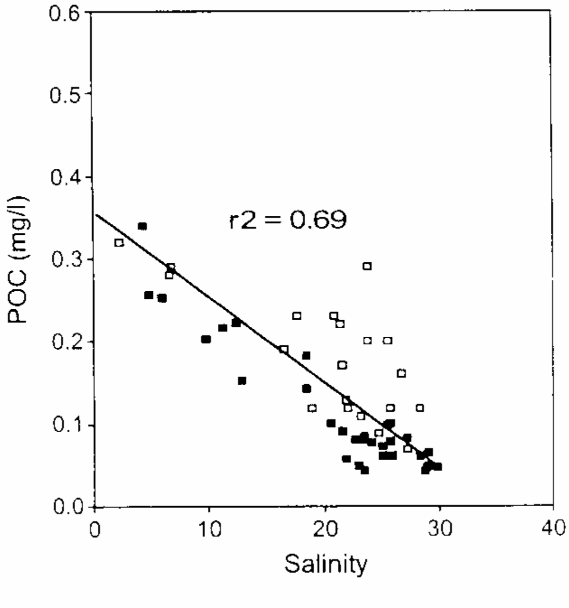


Figure 52 Distribution of POC against salinity in the Ob and Yenisey Estuaries: A. POC (µM) against salinity in the Ob Estuary: open squares – data from 2000, closed squares – data from 2001 (Gebhardt et al, 2004); B. 1993: Ob (B-1), Yenisey (B-2) (Shevchenko et al., 1997); C. 1999: Ob (C-1), Yenisey (C-2) (Gaye et al., unpubl.); B-C – symbols as in Fig.47,B

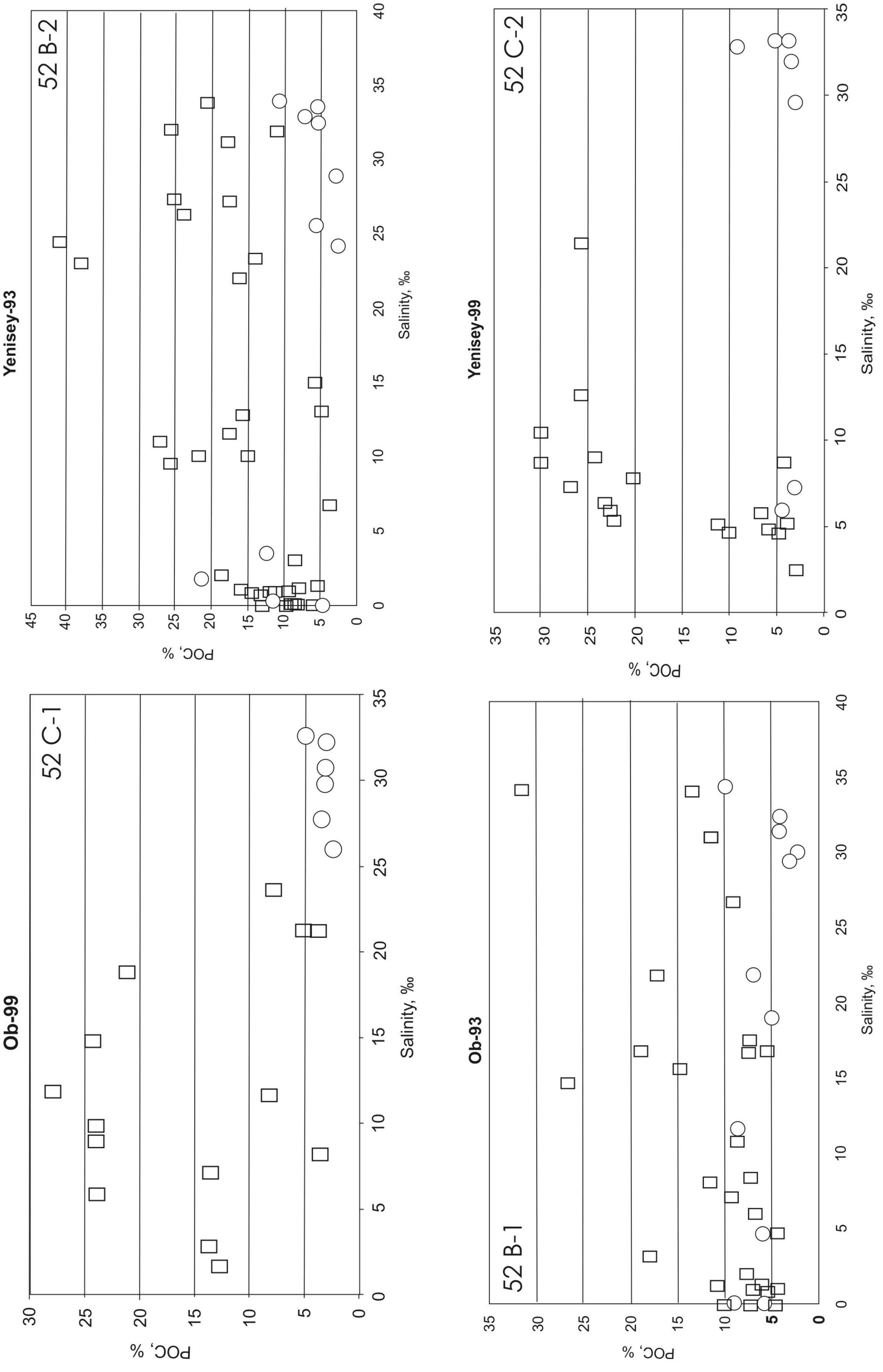


Figure 52 continued.

4.3.4.4 Nutrients

The particulate forms of N and P are measured very rarely. Here the distribution of P in SPM in Yenisey and Ob Estuaries are shown (BP-1999 and BP-2001) (Fig. 53 A). P_{SPM} plotted versus salinity for the Yenisey Estuary in 2000 and the Ob Estuary in 2001 (the data for the Ob in 2000 are absent) as well as in 1997 demonstrate a very monotonous distribution. The variations of $(P/Al)_{SPM}$ are in a narrow range from 0.02 to 0.09 in the Yenisey Estuary and from 0.03 to 0.19 in the Ob Estuary. In 2001, however, a significant increase of this ratio in the salinity range 12-29‰ has been observed in the Yenisey Estuary. Note, SPM samples with higher ratio were collected in the surface layer of water, while all samples with salinity 30-34‰ were obtained in near bottom layers. This means that in the Yenisey Estuary in 2001 the phytoplankton activity was probably higher than in previous year.

Fig. 53 B presents the distribution of PN versus salinity. Two sections in the Ob Estuary (1999 and 2001) and in the Yenisey Estuary (2000 and 2001) demonstrate the different behaviour of PN. An increase in PN in the Ob Estuary of up to 3-4.8% at salinity 6-18‰ and in the estuary of the Yenisey up to 4% at salinity 5-13‰ in 1999, up to 3-4.7% at salinity 18-27‰ in the Yenisey Estuary in 2000, very low PN concentrations in the Ob Estuary in 2001 (below 1%) and quasi-conservative behaviour of PN in the Yenisey Estuary in 2001 has been observed.

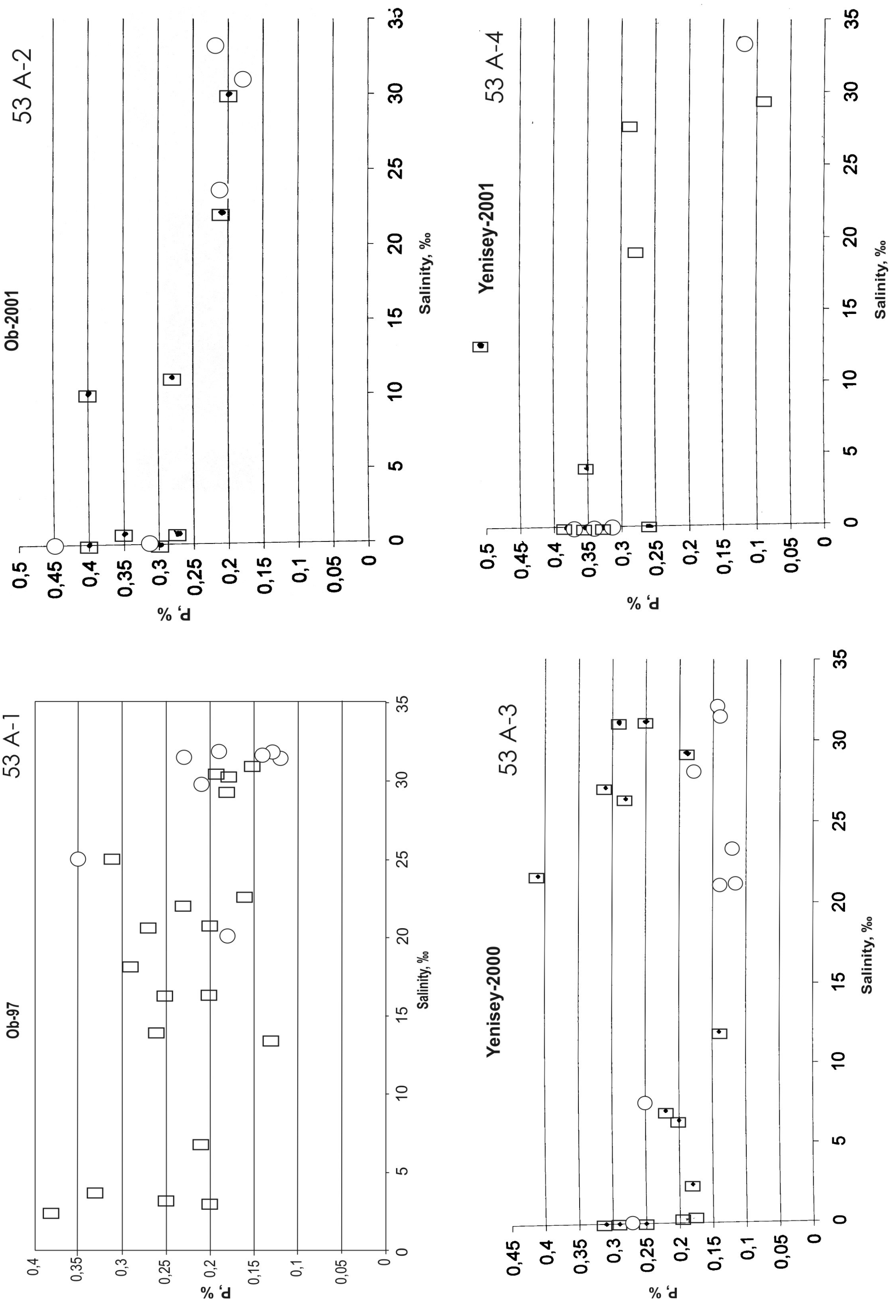


Figure 53 A. Distribution of P in SPM of the estuaries of Ob - 1999 (A-1) and 2001(A-2) and Yenisey – 2000 (A-3) and 2001 (A-4) against salinity. B. Distribution of N in SPM of the estuaries of Ob - 1999 (B-1) and 2001(B-2) and Yenisey - 1999 (B-3) and 2000 (B-4) against salinity.

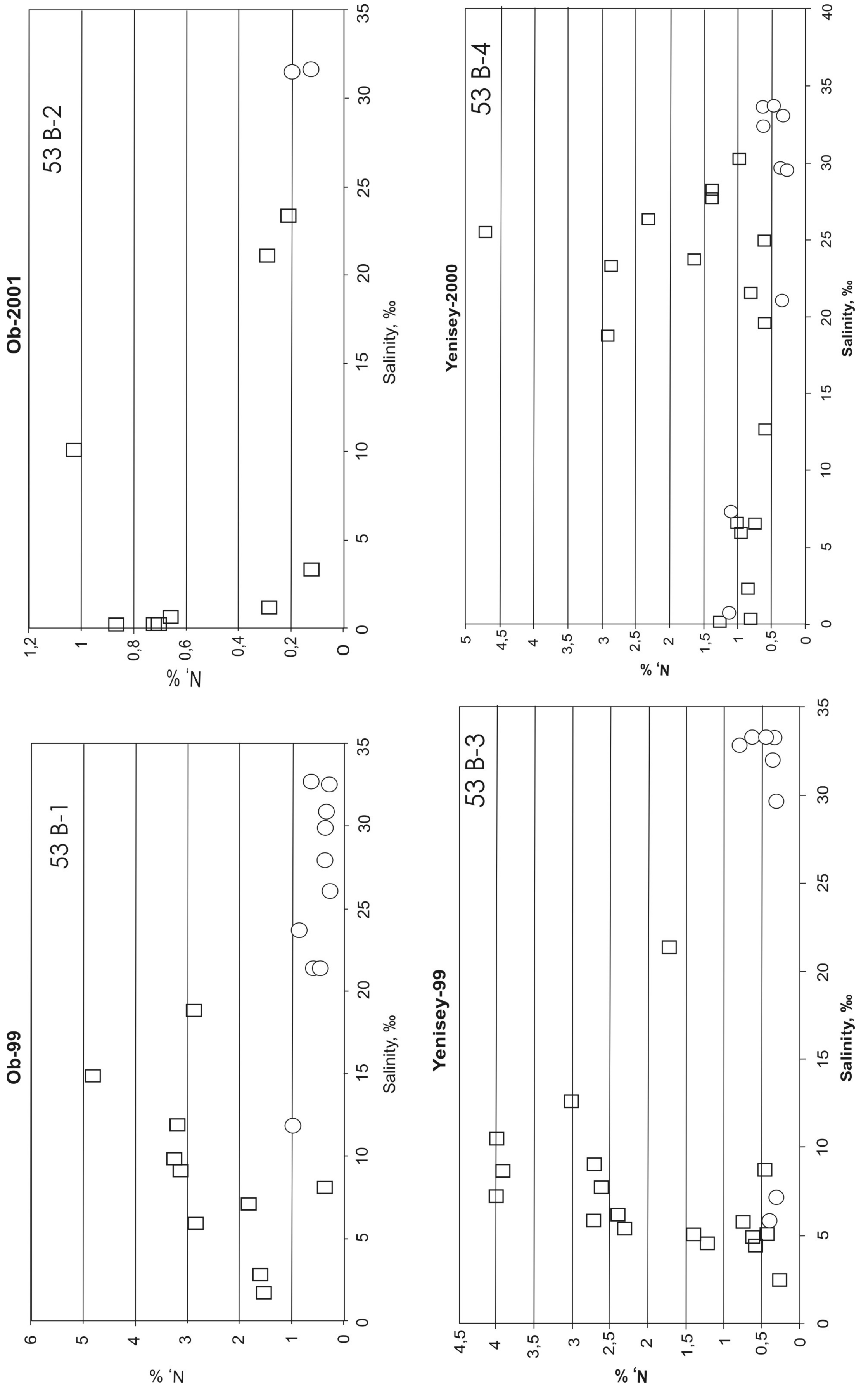


Figure 53 continued.

More informative is the C/N ratio (Fig.54). Soil and root material as major source of allochthonous SPM have C/N ratios of 18.3 and 25.0 respectively (the samples were collected about 100m away from the Ob River, approximately 5 km north of Salekhard from a birch forest (Unger et al, 2005)). Relative to this terrigenous material SPM in the Ob River near Salekhard revealed a C/N ratio of 9.4 which is near planktonic values and distinguishes SPM of this river from other arctic rivers (average C/N=11) (Lobbes et al., 2000; Unger et al., 2005). C/N ratio in the Yenisey Estuary with salinity near zero (BP-2000), where high abundance of bluegreen algae and chlorophyll a concentrations > 3µg/l were found (Noethig et al., 2003), was 7.5-7.6. Average ratio in surface SPM for both rivers (n=37) was 8.5, in the halocline (n=25) 9.7 and in deep water (n=36) 10.3 (Unger et al., 2005). These data help in the interpretation of the biogeochemical behaviour of trace elements in SPM of the rivers in the final section of this book.

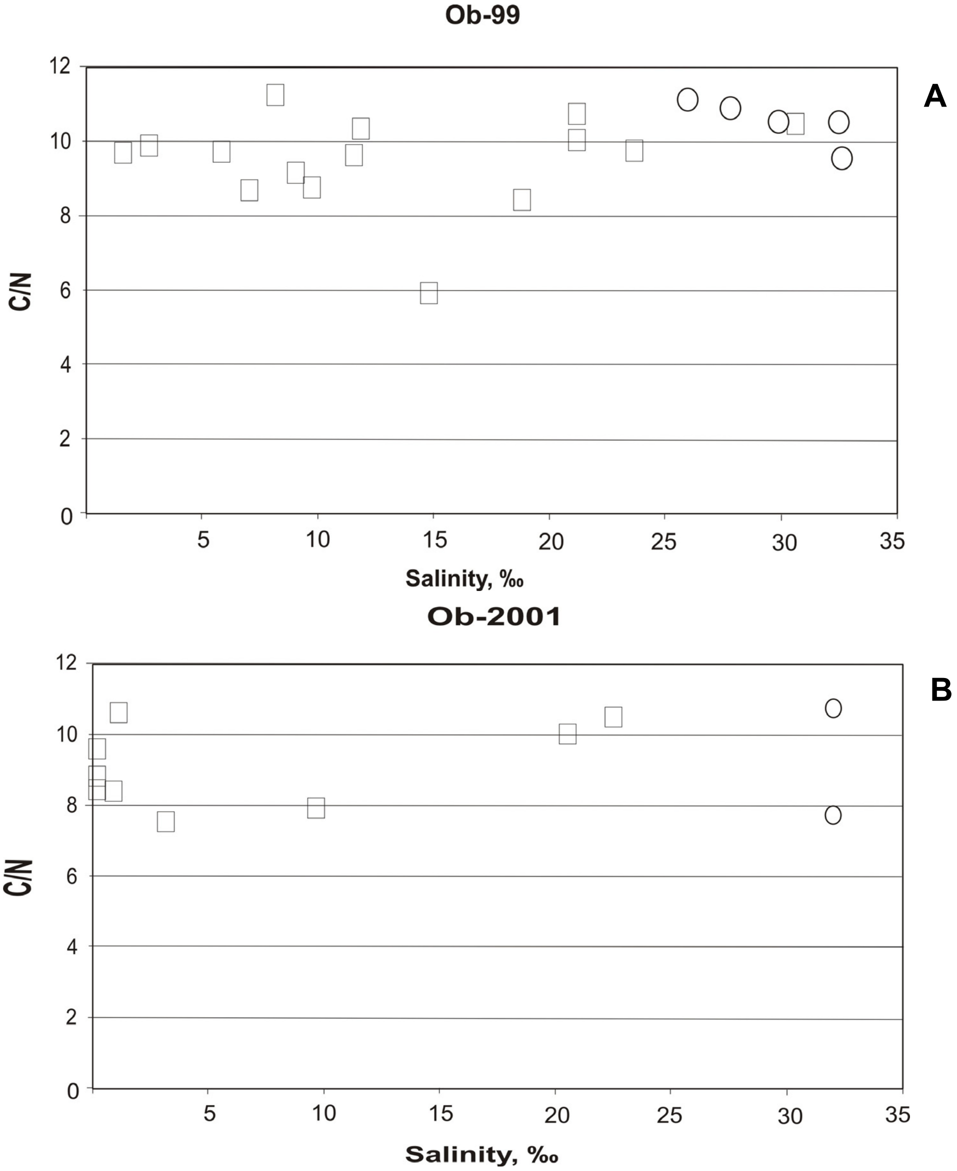


Figure 54 Distribution of the C/N ratio in SPM of the Ob (1999-A and 2001-B) and Yenisey (1999-C, 2000-D and 2001-E) Estuaries against salinity.

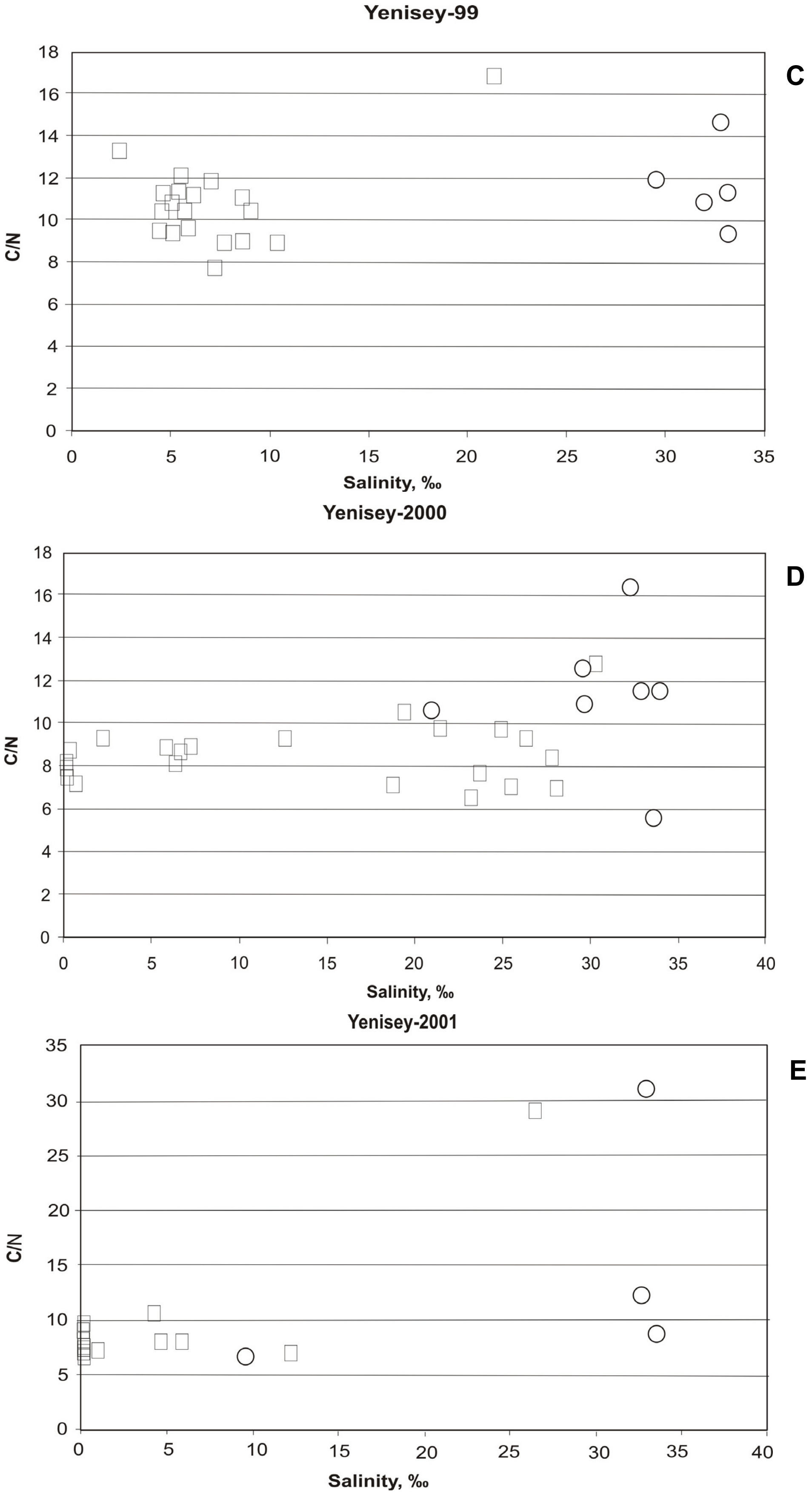


Figure 54 continued.

4.3.4.5 Trace elements

Because SPM differs in its organic content among the various water samples along the estuarine transects the element concentrations were calibrated against Al or Sc concentrations relative to their initial contents at zero-salinity as a function of increasing salinity. The line, taken as unit, corresponds to the original composition of the elements. The corresponding plots for SPM of the Ob and Yenisey Estuaries are discussed on the base of data of the DM-1993, BP-1999, BP-2000 and BP-2001 expeditions (Figs. 7, 8, 10 and 11). POC in centrifuged samples show that SPM samples of the Yenisey River were richer in organic matter in comparison to the Ob SPM (4.7% against 2.9%). As we have shown above (Fig. 52), POC increased with salinity in both estuaries: in the Ob Guba up to 4-5% at salinity 10-13‰ (unfortunately there were no SPM samples with higher salinity) and in the Yenisey Bay up to 12.5% (within a salinity range 12-22‰). The SPM samples of the DM-1993 expedition were analyzed by the INAA. Sc was analysed as well.

In the following, three Sc-normalized elements that characterize three groups of elements in accordance with the degree of their concentration in SPM are considered (Fig.55 A and Table 28) (Gordeev, 1998).

Group1. Lantanum, an element from the REE group, is a typical element of this group. It remains unaltered with changing salinity when compared to its content in river SPM. All other REE and also Fe, Zn, Hf and Th show similar behaviour in the mixing zone.

Group 2. Distribution of Sc-normalized chromium, a representative of this group, is stable up to salinity 10-15‰ and increases 5-7 times in concentration at higher salinity. This increase can be explained by higher photosynthetic activity of phytoplankton as a result of sedimentation of major part of river SPM and higher water transparency. Ba, Co and Cs show similar behaviour.

Group 3. A very high enrichment factor was demonstrated by Br (up to 36 in the Ob Estuary and 130-156 in the Yenisey Estuary). A significant increase at salinity of 5-12‰ for this element is observed immediately after the frontal zone 1. At the same time, there are the samples without any enrichment even at high salinity, the distribution is not homogenous and more data are required to find a suitable pattern.

The available data show that the biogenic factor plays an important role in the geochemistry of many elements in the river/sea mixing zone. Despite higher nutrient concentrations in the Ob Estuary these processes appear to be more intensive in the Yenisey Estuary due to higher phytoplankton activity and higher PP.

Data of the 28-th cruise (BP-1997) show the existence of three groups of elements according to their enrichment factors. Here, and in the following cruises Al, instead of Sc, was used for calibration (Sc was not determined).

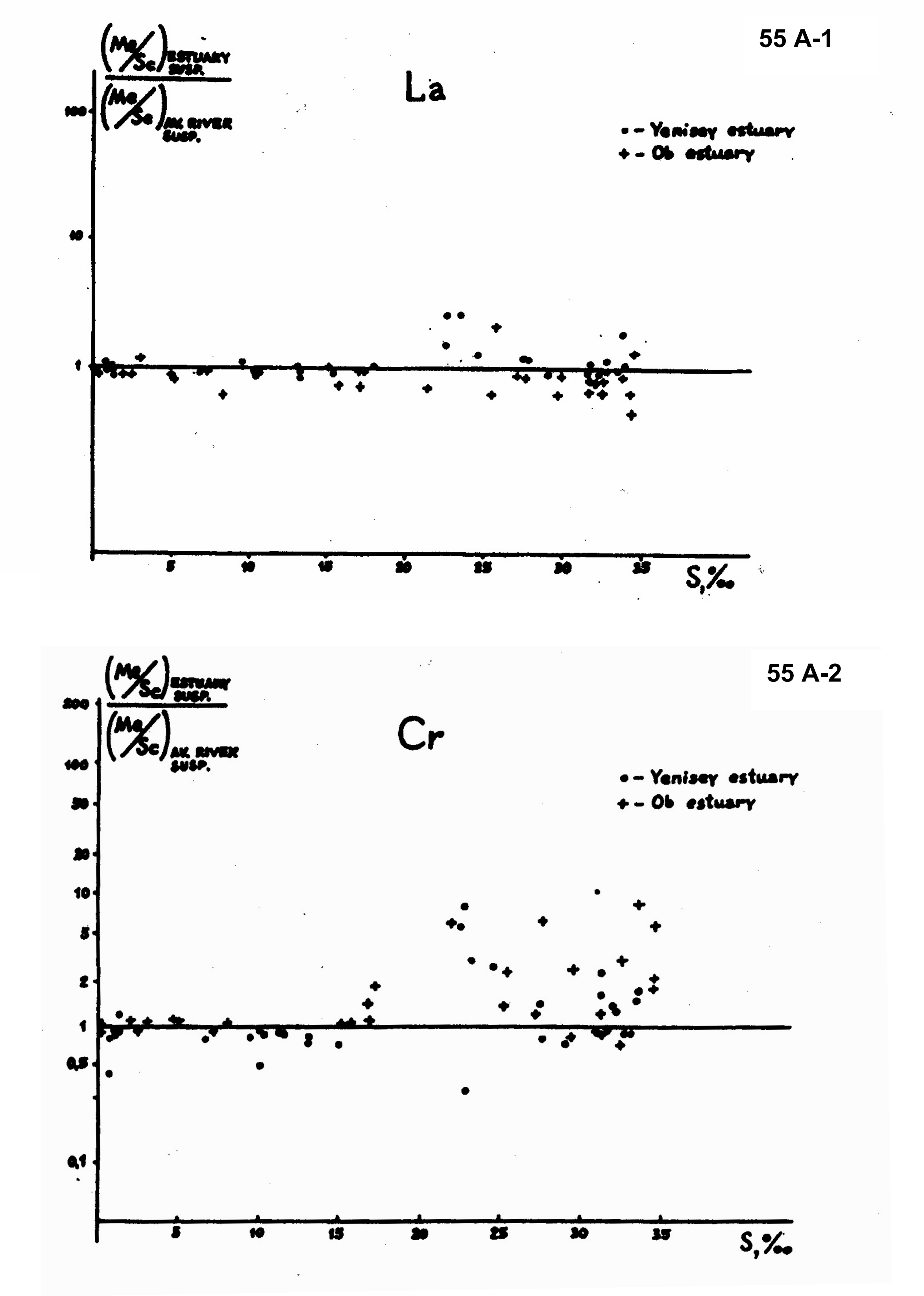


Figure 55 A. 1993 – Sc-normalized La (A-1), Cr (A-2) and Br (A-3) in the Ob and Yenisey Estuaries against salinity (Gordeev, 1998); B. 2000 – Al-normalized Cd, Co, Ba in the Yenisey Estuary (Beeskow and Rachold, 2003). C. 2001 – Al-normalized Cu, Pb, Cd, As (C-1) in the Ob Estuary and Ni, Cr, Ba (C-2) in the Yenisey Estuary, B-C- symbols as in Fig.47, B.

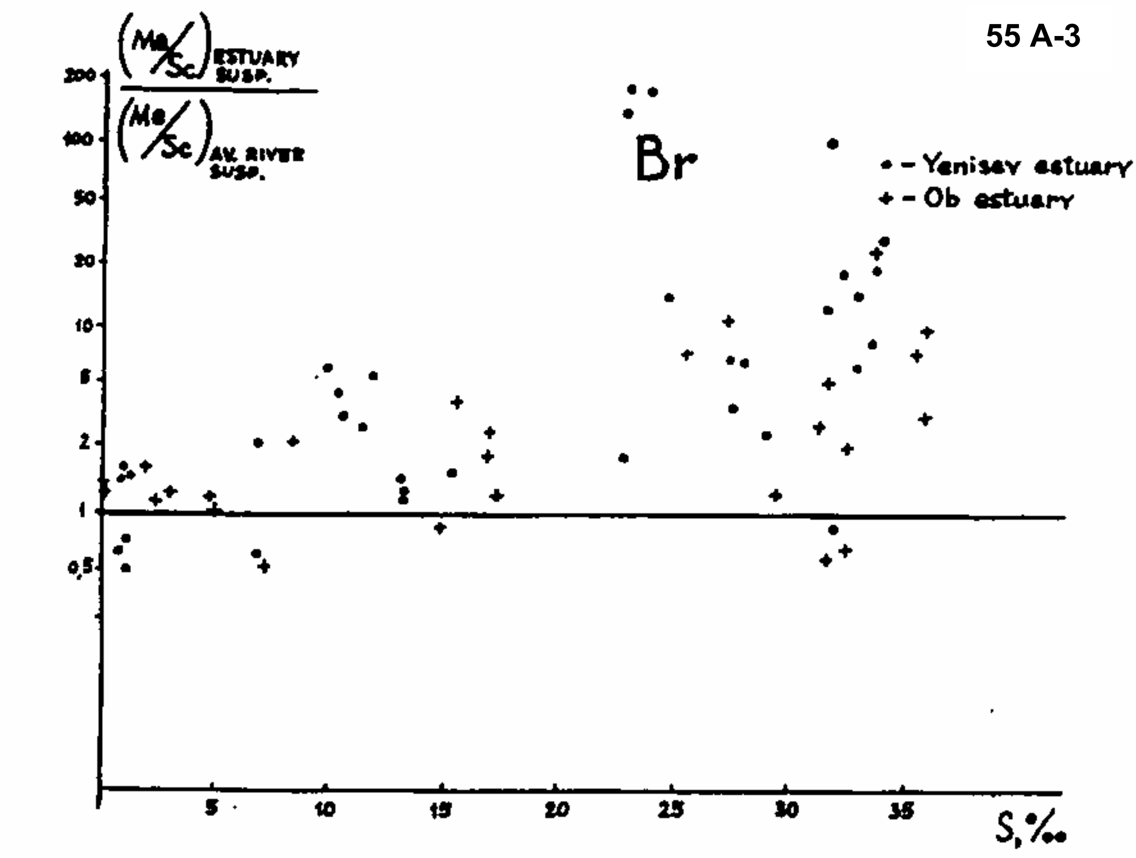


Figure 55 continued.

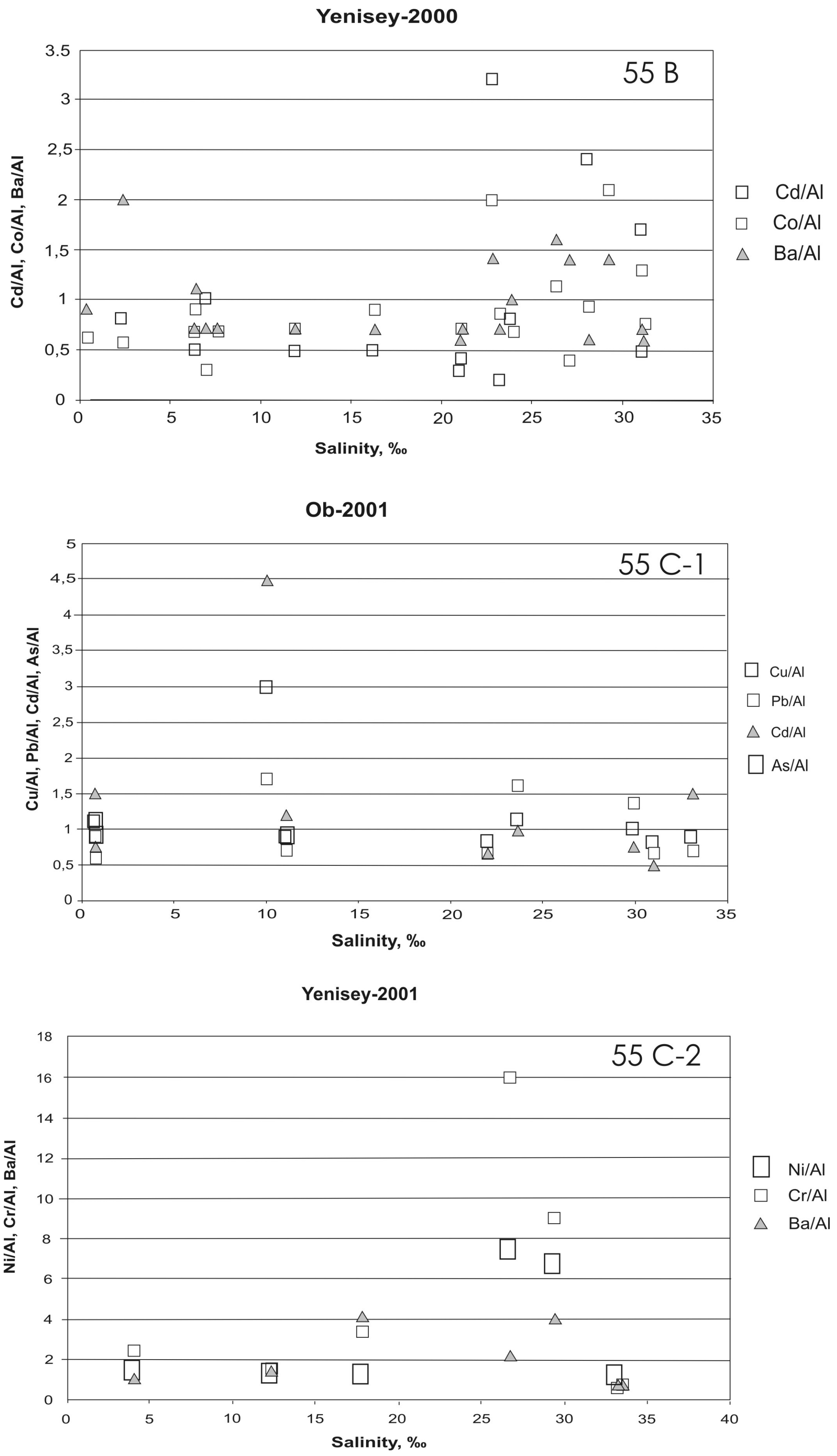


Figure 55 continued.

The Ob River:

Group 1. V, Ba, As – demonstrate quite stable behaviour (enrichment factor < 2);

Group 2. Cu, Zn, Ni – enrichment factor up to 6;

Group 3. Mn and Cr show the highest factor between 15 and 44.

The Yenisey River:

Group 1. V, Ba, Cr, Co, Pb – enrichment factor < 2;

Group 2. Cu, Zn, Ni – enrichment factor up to 6;

Group 3. Only Mn has the highest factor between 15 and 30.

In Fig. 55 B and Table 29 the behaviour of trace elements in the SPM samples in the Yenisey Estuaries (BP-2000) is shown. Here, again, several groups of elements in accordance to their behaviour were identified.

Group 1. U remains unaltered in the full range of salinity when compared to its content in the river SPM. This element follows the patterns of Fe, Mg and Ti.

Group 2. Zn, V, Ni, Y remain unaltered until salinity 20-23‰ and start to increase at salinity above 23‰ with low enrichment factors about 1.1-1.3.

Group 3. Co, Cd, As, Cu, Pb, Mn and Ba show the same behaviour as the elements of Group 2 but with higher enrichment factor up to 1.5-2.5.

The elements of the latter two groups follow the behaviour of Mn in the Yenisey Estuary. The ratios below unit for these metals at mid salinity coincide with high dissolved manganese concentrations and its redox sensitive behaviour (Beeskow and Rachold, 2003). The authors consider that desorption, probably caused by inorganic complexation with the major anions in seawater may explain this behaviour of the elements in the estuary.

The results of calculations for the expedition BP-2001 to the estuaries of both rivers are given in Table 30 and Fig.55 C.

In general, very different pictures in the estuaries were observed. In the Yenisey Estuary the enrichment factor is a moderate or high for the groups 2 and 3 with relatively low factors at salinity 12-17‰ and higher factors at salinity 26-30‰ (and no enrichments at salinity more than 30‰ because the SPM samples of near bottom layer), while in the Ob Estuary no enrichments were found for all the trace elements (except of only one sample at salinity 10‰ with factor in a range 1.5-7.0 for different metals).

Data on the behaviour of REE in particulate (and dissolved) form in the river/sea mixing zones of the Arctic rivers are very scarce. The experiments to define the degree to which REE removal occurs during mixing of river- and sea water have revealed that in river water with high POC concentration iron has flocculated together with organics and has caught predominantly HREE in this process (Hoyle et al., 1984). In an experiment, where river water was free of coarse suspended material, the fine particles were found to be rich in HREE. In natural environment, the hydroxide films are formed on quartz and other particles that may be probably enriched in HREE due to sorption from water resulting in high HREE concentration in the coarse particle fractions.

The REE concentrations were measured in two centrifuged SPM samples in the Ob (sample 02, salinity 10-23‰) and Yenisey (sample Y2, salinity 9-23‰) and during a river-sea transects at their seaward end (49-th cruise of the R/V "Dmitry Mendeleev"). The so-called coefficient of contrast (ratio $El_{>32\mu m}/El_{<4\mu m}$) in these two samples is more than a unit for the majority of REE's as it was shown for two river SPM samples (Fig.34). For the Yenisey transect the coefficient of contrast in river and sea samples (Y1 and Y2) are quite comparable while for the Ob transect the behaviour of sea sample (O2) is rather different compared to river sample (O1). The samples with highest salinity in the Ob transect were obtained when the ship was located in the western side of this transect (Fig.7). As it was shown in Section 4.3.3.1, the sample of the Ob SPM (O2) was not of predominantly river origin and had different mineralogy. This was considered to be the reason for the different REE behaviour in this sample compared to sample O1.

The shale normalized REE patterns in the Ob and Yenisey seaside SPM are given in Fig.35. There is no enrichment of LREE relatively HREE (La/Lu in samples O2 and Y2 is below 1). As shown for the river SPM samples (O1 and Y1) the distinction of REE behaviour of fine and coarse fractions are of quantitative character only, the general REE patterns are similar.

4.3.5 Net river fluxes to the Arctic Ocean

4.3.5.1 Definition of the net flux

The Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP, 1987) considers the *gross* river flux of dissolved and particulate substances into sea basins as the amount of substances transported by the river to the land/sea boundary (Section 4.2.3). The *net* river flux is determined as the amount of substances transported across this boundary. The boundary between the river and the sea is the area where no influence of seawater occurs, i.e. in a river cross section, where flow direction is unilateral.

The instant net flux of dissolved element E across an isohaline S at a time t may be written in the following form (Boyle et al, 1974):

$$F_t = Q_t \times ([E] - [S] \times d[E]/d[s])$$

where Q_t – freshwater discharge at time t,

E – concentration of the element of interest,

[S] – salinity.

If the relation between E and S is linear, than d[E]/d[S] is a constant and for any S in the linear range the expression in the round brackets is also constant and equal to the intercept $[E]_o$ of the straight line extrapolated from the linear segment. The net flux of the element through any isohaline in the linear range is then:

$$F_t = Q_t \times [E]_o$$

Normally, a linear regression technique is applied to obtain this intercept. It is used later to evaluate the net flux of dissolved element studied. The salinity range should include the isohaline through which the flux estimation is made.

This approach is acceptable for SPM and particulate element concentrations and also to estimate the net fluxes of SPM and some elements in Ob and Yenisey Rivers.

4.3.5.2 SPM

The most comprehensive data set on SPM concentration in the Ob and Yenisey Estuaries was obtained in the 49-th cruise of the R/V "Dmitry Mendeleev" (1993) (Shevchenko et al.,1996; Lisitzin, 1998). Here, these data are recalculated in the relationship to salinity (Fig.56 A). An exponential decrease of SPM concentration with salinity is observed for both estuaries. This decrease is more pronounced in the Ob Guba than in the Yenisey Bay because of higher TSM concentration in the river end member. In both estuaries a sharp decrease occurs at low salinity of 0-2‰ and a more gradual decrease at higher salinity. Figs. 56 B and C show the distribution of SPM with salinity during the expeditions BP-99 and BP-00. A generally similar trend with decreasing SPM concentrations and increasing salinity and high concentrations in near-bottom water due to re-suspension of bottom sediments is seen. Only the data of the BP-00 expedition reveal the constant SPM concentrations near 3.2 mg/l in the whole salinity range of the Yenisey Estuary. Gebhardt et al., (2004) combine the results of two expeditions (BP-00 and BP-01) and conclude that SPM behaves conservative in the Ob Estuary and is stable in the Yenisey Estuary. To our opinion, to combine the results of BP-00 and BP-01 expeditions is not correct. The authors themselves write that “due to the complex hydrographic situation in the Kara Sea, the datasets from different years couldn’t be merged”.

The near bottom SPM samples deviate from the general trends. The near bottom water is characterized by high salinity due to intrusion of sea water. High SPM concentrations are formed due to re-suspension of the bottom sediments. The GESAMP approach can be used to evaluate the net fluxes of SPM in the two arctic estuaries. The interception of the tangent to the marine end member with the y-axis (SPM concentration) occurs in a range of SPM concentrations between 2 and 4 mg/l in the Ob Estuary (Fig.56 A-1). The average SPM concentration for the river end member (n=10) was 37 mg/l. This means that in the MF zone of the Ob River about 89-95% of riverine SPM flux is deposited. However, the estimation is quite rough because of very few samples and absence of seasonal variations.

Fig.56 A-2 demonstrates the same relation for the Yenisey Estuary. The interception of the tangent with the y-axis is in SPM range from 0.3 to 0.9 mg/l. The average SPM concentration in river water is 4.4 mg/l and the SPM losses are between 80 and 93%.

These estimations are similar to those for several large world rivers such as the Amazon with 95% (Milliman et al., 1975), the Mississippi with 90% (Trefry and Presley, 1976), the Congo with 95% (Eisma et al., 1978), the rivers of the Black Sea and Asov Sea basins with 83% (Demina et al., 1978) and other.

The estimates obtained may be used to calculate the net SPM fluxes in the Ob and Yenisey Estuaries. These are about (0.8-1.7) x10^6 t/yr for the Ob and (0.3-0.94) x10^6 t/yr for the Yenisey.

In the Lena delta 83-90% of SPM are deposited (Alabyan et al., 1995) which is comparable to the losses in the Ob and Yenisey Estuaries.

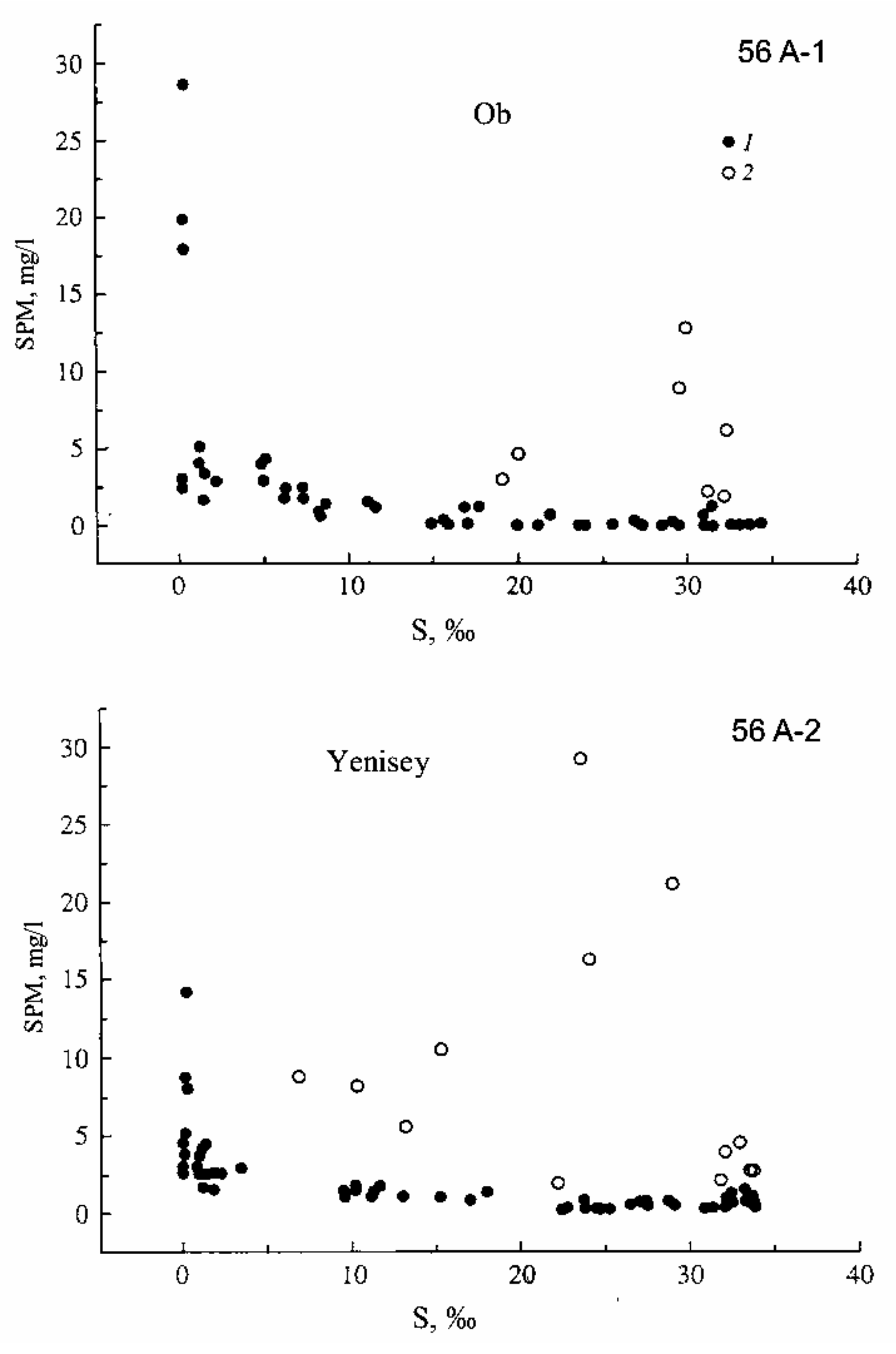


Figure 56 **Distribution of SPM concentrations in the Ob and Yenisey Estuaries against salinity: A. 1993: Ob (A-1) and Yenisey (A-2); B. 1999: Ob (B-1) and Yenisey (B-2); C. 2000: Yenisey. A-C- symbols as in Fig.47B.**

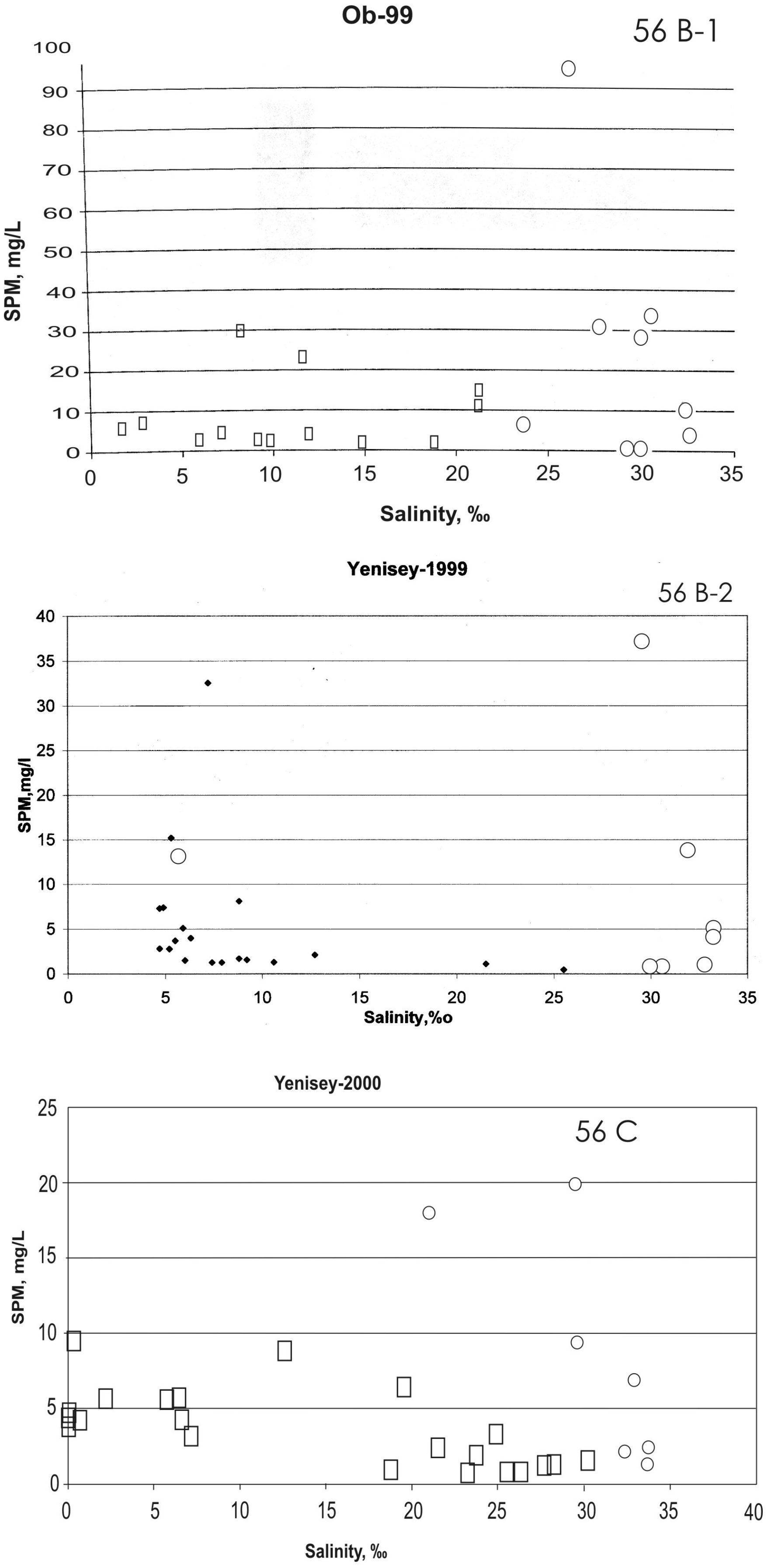


Figure 56 continued.

4.3.5.3 Major elements

It is possible to estimate the net fluxes for few elements only, due to very limited data. Furthermore, because of very complicated dependences of the concentration with salinity it is impossible to obtain reliable estimates for the so-called effective element concentrations for several elements (that is the concentrations obtained as the interception of the tangent with concentration axis).

The conservative behaviour of DOC in the arctic estuaries means that no real losses of DOC take place here (Kohler et al., 2003). For the POC concentrations as well as for dissolved and particulate nutrients, it is impossible to estimate the net fluxes at present.

The concentrations of dissolved major cations and anions in the Ob and Yenisey mixing zones vary linearly with no losses in the MF zones. This means that the net fluxes equal the gross fluxes. The results for the particulate suspended forms of major elements show that the elements normalized to Al or Sc are stable in the Ob Estuary (except Na which increased with salinity due to adsorption from sea water). Therefore, the loss of major elements in the mixing zone is assumed to be proportional to the loss of total SPM (89-95%).

In the Yenisey Estuary the situation is complicated. In 1993 and 2000, the Al or Sc normalized contents were stable in the MF (only Ca decreased and Na increased with salinity – Fig. 51 D), whereas in 2001 the enrichment factors for major elements in salinity range between 17 and 30‰ were detected.. However, at salinity above 30‰, near estuary-sea boundary, the enrichment factor was again near unit for all the elements. In the first approximation, we may accept the same approach as for the Ob Estuary and the loss of major elements is assumed to be proportional to the loss of SPM (80-93%).

The results of calculations are given in Table 31. Si and Al are omitted due to the reasons mentioned above, Na because of its complicated behaviour in the estuaries and Fe and Mn are considered as the trace elements It is assumed for the gross fluxes that the major elements Ca, Mg, K and Na are transported in dissolved form (88-99%). Predomination of these elements transportation in dissolved form is even more significant for the net fluxes (more than 99%) because of great loss of SPM in the estuaries.

4.3.5.4 Trace elements

To calculate the net fluxes of dissolved elements it is necessary to evaluate the effective dissolved concentrations for the lower courses of the rivers. They are depended on the behaviour in the mixing zone. The effective concentrations are equal to the average concentrations in the lower river in the case of conservative behaviour. They are lower when the element has significant losses, for example due to flocculation, and they are higher than the factual concentration in river water when desorption from SPM takes place for this element.

The effective concentrations were established based on available data for the Ob and Yenisey Rivers (Dai and Martin, 1995), for the Lena River they were estimated in the work of Guieu et al. (1996). These results are limited, and it is not possible to evaluate its effective concentration for dissolved Cd due to its significant variability in the mixing zones of the rivers. The effective concentrations are the following (in µg/l):

Ob – Fe – 31.4, Cu – 2.09, Ni – 1.76, Pb – 0.005;

Yenisey – Fe – 18.5, Cu – 1.78, Ni – 0.87, Pb – 0.004;

Lena – Fe – 3.6, Cu – 1.70, Ni – 0.70, Pb – 0.05, Zn – 0.08, Cd – 0.034

(corrected estimations from Dai and Martin (1995) for the Ob and Yenisey, and from Guieu et al. (1996) for the Lena in accordance with new dissolved concentrations (Table 8)).

The effective river end member for Ba_{diss}.was estimated by extrapolating to zero salinity of the linear Ba-salinity relationship observed at high salinity (Guay and Folkner, 1998). Estimated effective concentrations are the following: Ob- 13.7 µg/l, Yenisey- 17.1µg/l, Lena - 17.8µg/l, Mackenzie - 71µg/l.

The comparison of calculated and measured concentrations shows that the effective concentration of $Fe_{diss}$is one order lower of its actual concentration. The values are comparable for Pb, Cu and Ni. The net flux of these elements is calculated by multiplying effective concentrations to multi-annual river discharges.

Similar situation is observed for the trace elements. The assumption that the losses of suspended trace metals in the MF zones are determined mainly by the losses of SPM itself is accepted here as well. The results of calculations are shown in Table 32. The comparison of net to gross fluxes shows that the ratios are more variable for dissolved metals (from 0.11 for Fe to 3.2 for Ni in the Lena MF), while for the suspended forms the variation is small (0.08-0.13 for three rivers, and 0.1 as average for total Eurasian Arctic). This is because the dissolved elements demonstrate very different behaviour in the mixing zones, whereas the variation of suspended metals is small.

In general for the Russian Arctic, the net flux of Fe_{diss} is 5 times less than its gross flux, for Pb_{diss} the net flux/gross flux ratio is 1.2, for Ni_{diss} 0.81 and for Cu_{diss} 1.1. These elements in particulate form vary between 0.09-0.11. The net fluxes of total elements (the sum of dissolved and suspended forms) comprise about 10% for Fe and Pb, about 40% for Ni and 60% for Cu of their gross fluxes that penetrate into the open ocean.

4.4 Geochemistry of the estuarine bottom sediments

4.4.1 Facial environments

The facial analysis of recent marine and oceanic sediments is one of the most important instruments for marine geochemists who investigate the lithology of sea bottom sediments. Among the main facial indications there were usually the colour of sediments, grain size, mineralogical composition (light, heavy and clay minerals), concentrations of some chemical components and elements ($CaCO_3$, SiO_2 opal, Corg., Fe, Mn and other) investigated.

The facial structure of surface bottom sediments in the Ob and Yenisey Estuaries and the adjacent areas of the Kara Sea were studied in the 49-th cruise of R/V “Dmitry

Mendeleev" and in the joint Russian-German expeditions on board of R/V "Academic Boris Petrov" (1997, 1999, 2000, 2001, 2002, 2003). A number of new facial indications were used in these investigations such as some biogenic remains (dinoflaggelates, diatoms, foraminifers), petrographic composition of the fractions 63-125µm, the rates of sedimentation and a wider range of chemical elements.

There are many publications with data on lithology, granulometric and mineralogical composition of sediments (Levitan et al., 1996; Muller and Stein, 1999; Levitan et al., 1999; Levitan, 2001; Bourtman and Levitan, 2002; Steinke, 2002; Levitan et al., 2002 and other), biogenic remains (Matthiessen, 1999; Polyakova, 2003; Khusid and Korsun, 1996), the rates of sedimentation (Stepanets et al., 2002,2004). An overview of all works was published recently by Levitan et al. (2005). The authors define facial environments with different type of the Upper Quaternary deposit structure such as the river deposits proper environment, the facial environments of the Ob and Yenisey Estuaries, the facial environments of the inner shelf- the Ob-Yenisey shoals, and the facial environments of the zone of intensive accumulation of very fine clayey muds. The increasing density of the grid of geological profiles, and the widening of the geographical frames of the studied area allowed to increase the set of facial environments and gives more detailed description of the environments (Levitan, 2001, 2002; Levitan et al., 2005). In the following, the main results of these works are presented.

The facial environments of the lower courses of Ob and Yenisey Rivers, Estuaries and the adjacent Kara Sea are shown in Fig. 57. There are four main facial environments: the river facial environment which includes the lower reaches of the Taz, Ob and Yenisey Rivers (code A), the facial estuarine environments of the Ob and Yenisey Rivers (code B), the facial environment of the inner shelf (the Ob-Yenisey shoals) (code C), and the facial environment of the external shelf including the Voronin and St. Anna troughs (code D). In the next sections a very short description of the facial environments will be given with more information about grain-size composition, mineralogy and chemical composition of bottom sediments.

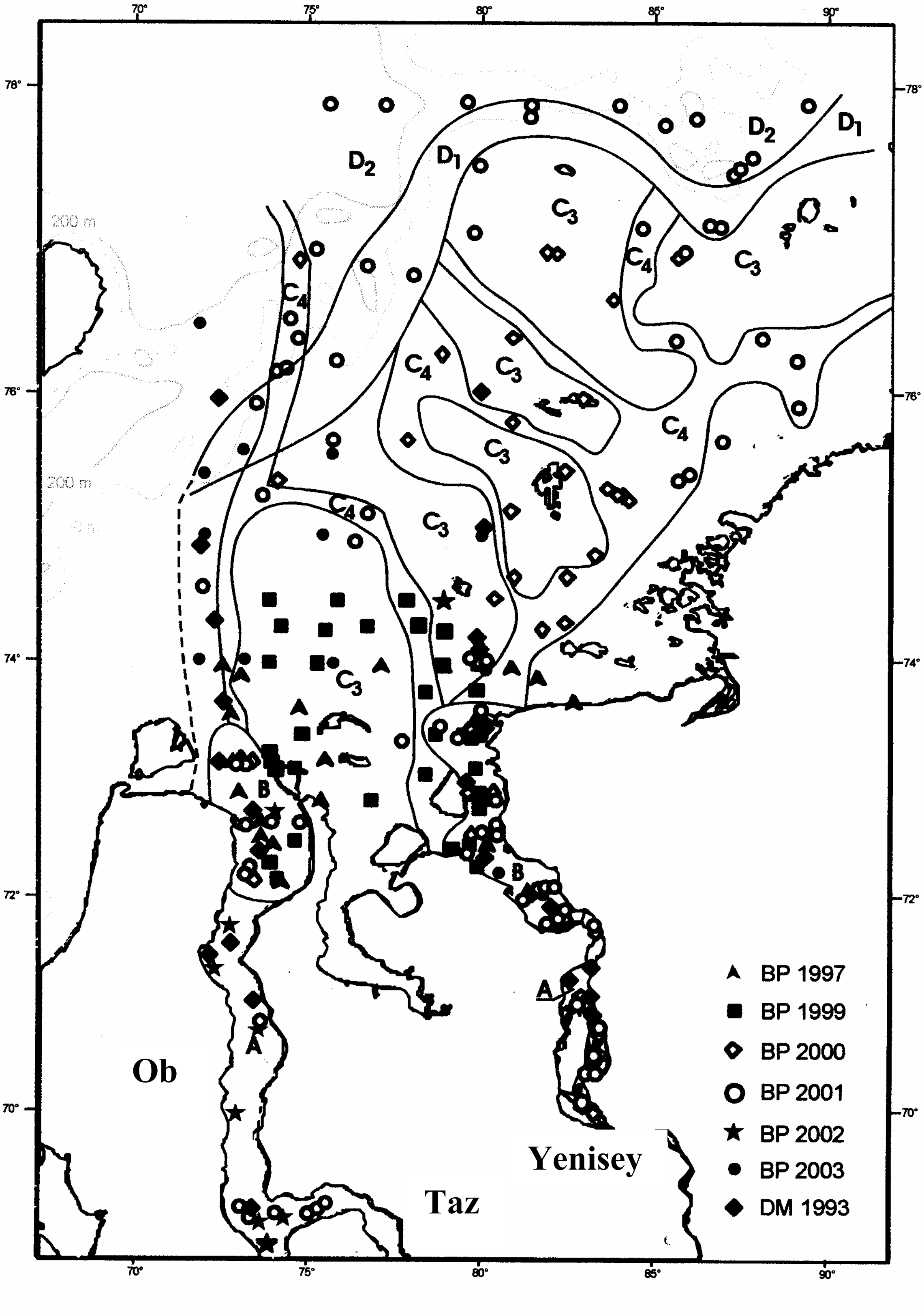


Figure 57 Facial zonality and location of geological stations in the eastern Kara Sea: BP – R/V "Akad. Boris Petrov", DM – R/V "Dmitry Mendeleev" Numbers = years, A-D- facial zones (Levitan et al., 2005).

The river facial environment (Fig.57 code A) is characterized by fresh water composition. As a rule, the thickness of the loose deposits is low (few tens of cm) and only at confluence of the Taz and Ob Rivers it is about 2-3 m. The great variations of water and SPM supply are typical for the rivers (see section 4.1). Significant differences in geological structure of the Ob and Yenisey catchment areas – the loose Neogene Quaternary deposits of the West Siberian platform in the Ob basin and in the left tributaries of the Yenisey River, and the rocks of the ancient East Siberian platform, with the Putorana Plateau in the lower course of the Yenisey River (see section 2.1) results in some differences between the river facial zones.

The facial environments of the Ob and Yenisey Estuaries are limited by the appearance of sea water and the sharp hydrological front with salinity of surface waters near 20‰. The bottom is flat with the thickness of the Holocene deltaic sediments up to 20-30 m. Near the sides of the estuaries there are narrow and deep lowerings with sharp decrease of the Holocene sediment thickness (down to few meters). All processes typical for the MF take place in these facial zones: sedimentation of relatively coarse material in the proximal part (code B1) and physico-chemical and biological processes connected with sedimentation processes dominate in the distal part (code B2).

The facial environments of the inner shelf occupy the Ob-Yenisey shoals down to a depth of 50-60 m. This shoal is the gentle underwater plane (code C3) with very small incline to the north. There is a group of the island archipelagos (Izvestia of CIK, Academy of Sciences and other), and also the flooded hydrographic network of the pra-Ob and the pra-Yenisey Rivers (code C4). The largest area of the Ob-Yenisey shoal presents the erosional or accumulative-erosional surface formed by combination of recent elevations and active erosion near bottom currents (Gurevich, 1995). Therefore, the thickness of the loose deposits here does not exceed the first tens of cm and is occasionally reduced to zero, with outcrops of the basal rocks.

In their lower courses the valleys of the pra-Ob and pra-Yenisey Rivers cross the slope of the Ob-Yenisey shoal (Fig.57). A part of channels are filled with sedimentary material (the Holocene thickness of up to 10 m) (Stein, 2001; Dittmers and Schoster, 2004). The dominated erosion processes on the main part of the Ob-Yenisey shoal lead to outflow and re-deposition of fine pelitic material in the flooded channels and shelf deeps which serve as the sedimentary traps. At the same time, these channels are used as the transport ways of sediments into the nepheloid layers. At these conditions the material from bottom erosion has a prevailing role while the river sediments are of subordinate importance.

The facial environments of the external shelf are considered here only shortly. They are located in the transitional zone between the Ob-Yenisey shoals and deeper areas of the transversal Voronin and St. Anna troughs (code D1) and also in the troughs themselves (code D2). The paleo-relief of the slope and the foot is much dissected, and almost totally overlapped by the Holocene sediments of 3-7 m thickness.

4.4.2 Facies and grain-size composition

The river facies include the channel alluvium and sub-aquatic-deltaic deposits. They are characterized by gray or greenish-gray colour. In the zone A the sediments are very diverse in grain-size composition. Depending on hydrology they vary from gravel-sandy deposits to sandy clays (Table 33). Normally the river sediments of the Yenisey are characterized by a bi-modal distribution with maxima at about 20 and 400µm (Fig.58). The method of elutriation conforms the bi-modal distribution in sediments of the river facies (station 4417- Ob, and station 4409- Yenisey) but there is a shift in grain size (the picks at >50 and <4 µm). At St. 4417 the bottom sediments were mainly sands with fraction >50µm 67.8%.

The estuarine sediments are very specific in their grain-size composition. In the proximal facies (B1) they are typical the silty-sandy clays while in the zone B2 it is monotonous fine pelitic clays of olive-gray or black colour. In the Yenisey zone B2 at station.23 (Fig.32) we see again bi-modal distribution but with more uniform pattern with maxima between 10 and 100µm (Beeskow and Rachold, 2003).

The bottom sediments of the inner shelf (the Ob-Yenisey shoals) differ significantly depending on their accumulation places: in paleo-river valleys and shelf deeps (C4), or on the "shoulders" of the river valleys (C3).

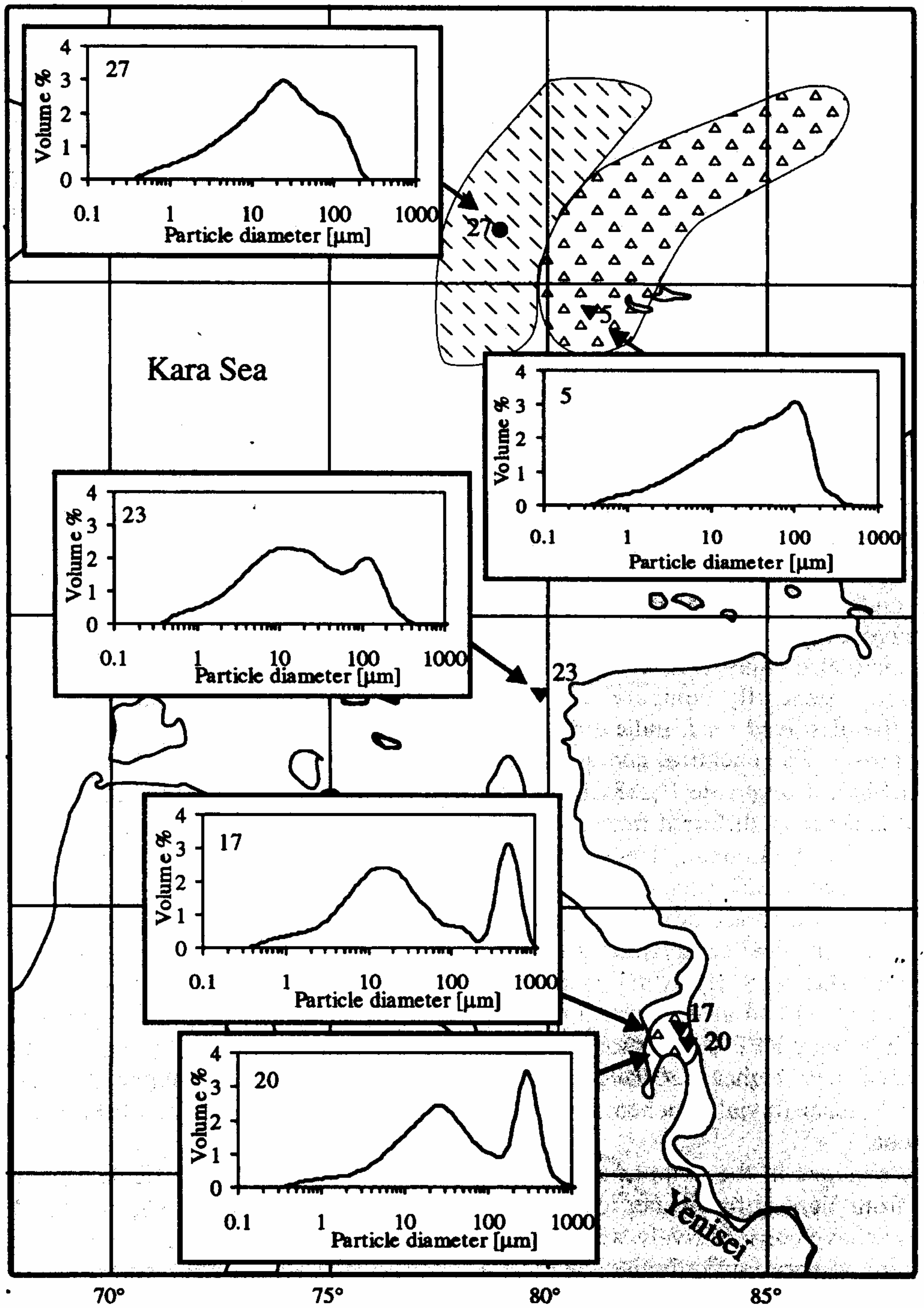


Figure 58 Grain-size distribution of surface bottom sediments of the Yenisey River and Estuary and the inner Kara Sea (Beeskow and Rachold, 2003).

4.4.3 Mineralogy

River facial environment (A)

The illite-smectite complex of clay minerals dominates in the fraction < 2µm in the Ob surface bottom sediments, kaolinite and chlorite take the subordinating role (Table 11). The river Taz is a local source of chlorite (Levitan et al, 2005). After confluence between Taz and Ob this mineral is mixed with other clay minerals. Distribution of clay minerals in the surface bottom sediments of the southern Kara Sea, including the Ob and Yenisey Estuaries, is shown in Fig.59. The sediments of the Yenisey River are enriched by smectite and, in lesser degree, by kaolinite, and contain low concentrations of illite in comparison to the Ob sediments (Steinke, 2002).

The ratio smectite+kaolinite/illite = SKI seems to be a very useful proxy to distinguish the Ob and Yenisey SPM by the clay mineral composition (Stein et al, 2004). The surface sediments of the Yenisey Estuary are characterized by SKI>2.5 while the Ob sediments display a SKI< 2.5 (Fig.60). High SKI was found in the depressions towards the NNE with high clay content in bottom sediments. High SKI in sediments west and north-west of the Yenisey Estuary are related to distribution of fine-grained material transported by currents from the Yenisey Estuary (Stein et al, 2004).

Among light minerals in fraction 0.1-0.05 mm the potassium feldspars and quartz prevail. The same minerals dominate in this fraction of the Yenisey sediments also. The ratio Q/FS is 3.3 for both rivers (Table 34). Among heavy minerals the complex of epidote-black ore minerals- clinopyroxene dominates in the Ob sediments, the Yenisey sediments are enriched by clinopyroxene. The coarse fraction 63-125 µm and >125 µm are enriched by the plant remains and the rock fragments in the sediments of both estuaries. Distribution of minerals in bottom sediments of the Yenisey River is very irregular. The sediments collected on distance less than one km from each other quiet often are presented by significantly different lithotypes (Levitan et al, 2005).

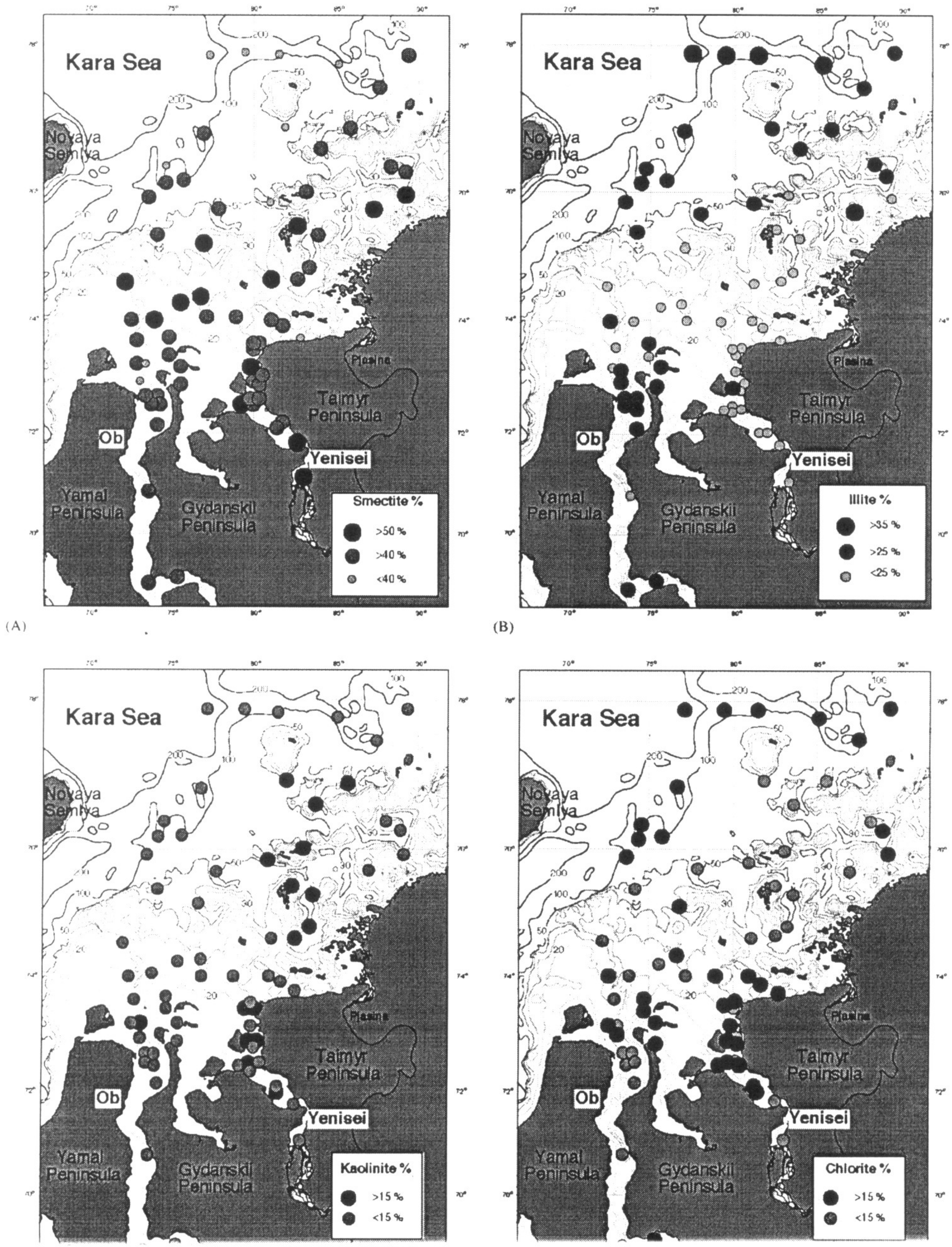


Figure 59 Distribution of clay minerals (in % from total) in the surface bottom sediments of the Kara Sea, including the Ob and Yenisey Estuaries (Stein et al., 2005).

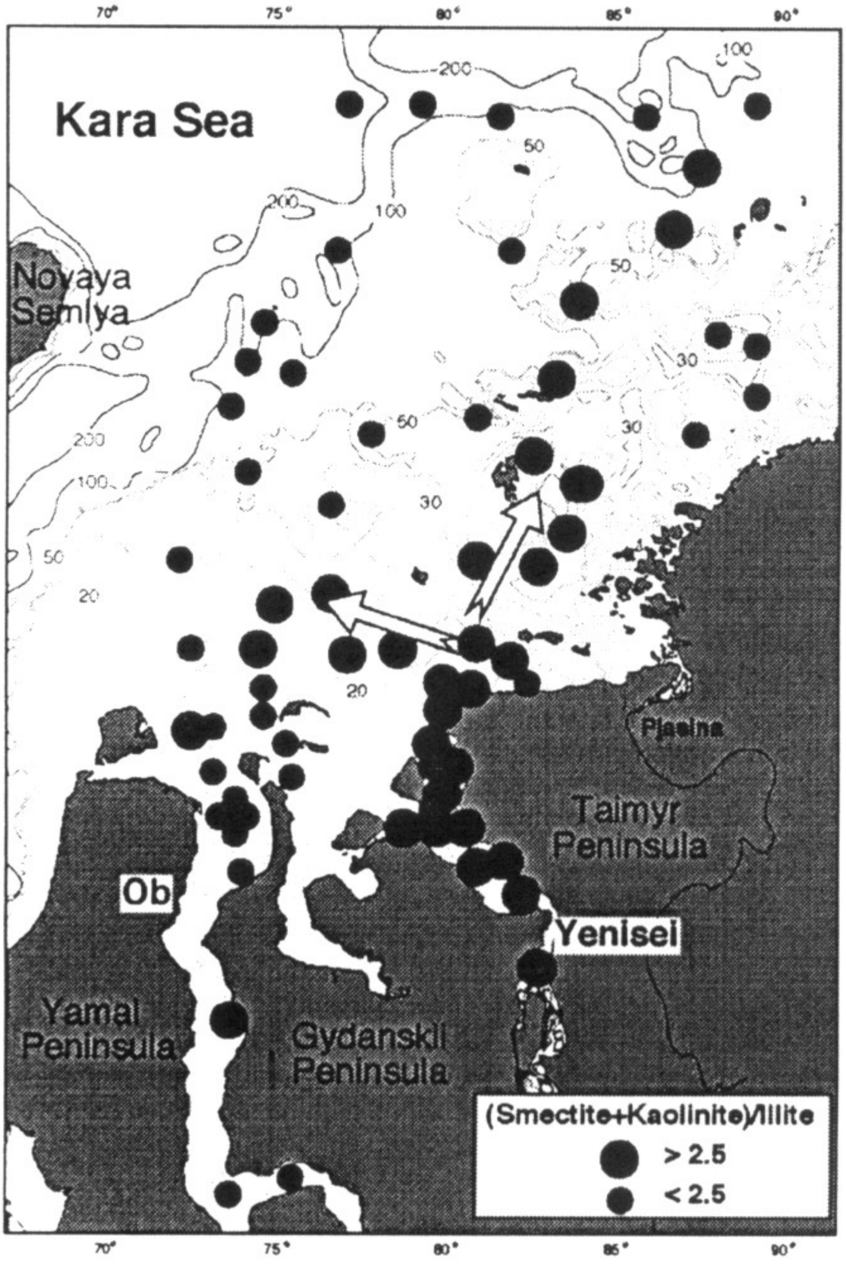


Figure 60 **The ratio smectite + Kaolinite/illite (SKI) distribution in the surface bottom sediments (Stein et al., 2004).**

Estuarine facial environment (B)

In general the composition of minerals in bottom sediments of the Ob and Yenisey Estuaries is very similar to that in the river facie (A), especially for clay minerals (Table 35).

In fraction 0.1-0.05 mm the complex of light minerals differ from alluvium by lower content of quartz and Q/FS ratio only.

The river complex of heavy minerals keeps its dominating role here but to the northern boundary of the Ob and Yenisey MF's increases the content of clinopyroxene, hornblende, garnet and Cl/Ep ratio, and decreases the content of epidote and black ore minerals (Table 36).

In fraction >125µm there are many plant remains and polychaets (Levitan, 2002).

Facie of inner shelf (C)

The clay mineral composition of bottom sediments of this facie is practically the same as in previous facies but the content of illite increases and smectite decreases in the northern direction. Near the northern part of the Taymyr peninsula the concentration of illite and kaolinite is relatively higher, and of smectite is lower in comparison to other parts of this facial zone.

Among the light minerals is dominated quartz and the ratio Q/FS is high (Table 34). It is worthy to note that the typomorphose features of quartz in bottom sediments of the Ob-Yenisey shoal differ significantly from the characteristics of the quartz grains in facial zones (A) and (B) (Levitan et al., 2005). The source of quartz in the deposits (C) is the basic Mesozoic ores while in alluvium and estuarine sediments quartz of far-distant river transport prevails.

Deposits of the facie (C3) are relatively enriched by black ore minerals, hornblende and garnet while clinopyroxene concentration and ClP/Ep are reduced (Table 36). In fraction >125 µm is low the content of rock fragments, among the biogenic remains the polychaets prevail on the Ob traverse, near the Taymyr coastal zone there are many agglutinated benthos foraminifers, and on the most area of this facie – bivalves molluscs (Levitan, 2002).

The fine pelitic silts in the facie (C4) contain the same complex of clay minerals as in the facie (C3) because of they are transported mainly in surface water masses and deposited to the bottom from the same layer. Smectite content along the Yenisey cross-section is higher than on the Ob cross-section (Fig.59).

The light minerals in fraction 0.1-0.05 mm form the similar complex in both facies (C3) and (C4). In (C4) the concentration of clinopyroxene and ClP/Ep ratio are a little higher than in (C3), may be due to the input of river material. Fraction > 125 µm is much lower here and its composition is very stable (Levitan, 2002).

Facies of external shelf (D)

There are some differences in the complex of clay minerals here. The contents of illite and smectite are equal (D2), and chlorite is higher than kaolinite (Steinke, 2002). The sediments of facie (D1) related to the contents of quartz and sum of feldspars are similar to the sediments of the mixing zones (Table 34). The concentration of clinopyroxene is lower, and of epidote and garnet is higher than in facie C. In fraction > 125 µm is higher the concentrations of black ore minerals and rock fragments (Levitan and Krupskaya, 2003). Among the biogenic remains in this fraction dominate the polychaets in the eastern part, and agglutinated benthic foraminifers in the western part of this zone.

4.4.4 EPXMA of bottom sediments

The electron probe X-ray micro-analysis (EPXMA) was applied to study the surface bottom sediments of the Yenisey River and Estuary in work (Jambers et al., 1997).

In this study 12 sediment samples which cover the whole estuarine system were collected in 1993 (the 49-th cruise of R/V "Dmitry Mendeleev") (Fig. 7). Only two sediment samples at Sts. 4408 and 4412 were of the sand type, another 10 samples were belonged to silt and clay fractions.

The Fe-rich alumino-silicates and Fe-alumino-silicates are the major particle types in bottom sediments of the river and its estuary. The total abundance of these Fe-containing alumino-silicates varies between 40% and 83%. There are also the pure alumino-silicates and alumino-silicates with some K and/or Ca.

Fe-rich particles are only found in the fresh water zone and in a part of the estuary (Sts. 4405 to 4413), a decreasing trend was noted from the river to the open sea. This fact points to an inflow of suspended Fe-rich particles by the river and probably due to flocculation of Fe-organic colloids in the river/sea mixing zone which are deposited within the estuary.

Small number of Ti-rich particles were detected in three samples only (stations 4411-4412 in the estuary and station 4493 in the open sea), although the number of Ti-rich particles was relatively high in all filtered suspended samples. These particles in bottom sediments probably originate from sedimentation of Ti-rich suspended particles. However it was surprising to note that this type of particles was completely absent in bottom sediments at St. 4403, while in suspended matter on this station there were up to 50% of particles contained Ti. The authors (Jambers et al., 1997) consider that since TiO2 is very insoluble in water, the only possible explanation for the lack of Ti-rich particles in the sediments is that these particles are too small (0.6-1.1 µm) to undergo sedimentation.

4.4.5 Magnetic susceptibility (MS)

MS may serve as a very useful instrument to distinguish between different source areas of terrigenous sediments. The ferromagnetic minerals have a significantly higher susceptibility than most other common minerals. Therefore the changes in susceptibility are controlled by variations in the content of these minerals (mostly magnetite, titanomagnetite or maghemite). Volcanic rocks due to higher content of ferromagnetic minerals have much higher MS than other rock types.

MS was measured in surface sediments of the Ob and Yenisey Estuaries and in adjacent Kara Sea (Stein et al., 2004). The porosity-corrected MS values of surface sediments have shown (Fig.61) that the values for the Yenisey Estuary were significantly higher than in the Ob Estuary (in average 3000-4000x 10^{-6} SI in the Yenisey against < $1000\text{x}10^{-6}$ SI in the Ob). This fact was noted by Levitan et al (2005) also.

High MS values in the Yenisey Bay are the result of specific features of the Yenisey SPM, a major source of which are the widespread Triassic plateau basalts and tuff deposits of the Putorane massif (Duzhikov and Strunin, 1992; Stein at al., 2004). Basalts and their weathering products are generally characterized by high MS values. At the same time the sediments supplied by the Ob River drained the Siberian lowlands are characterized by much lower MS values.

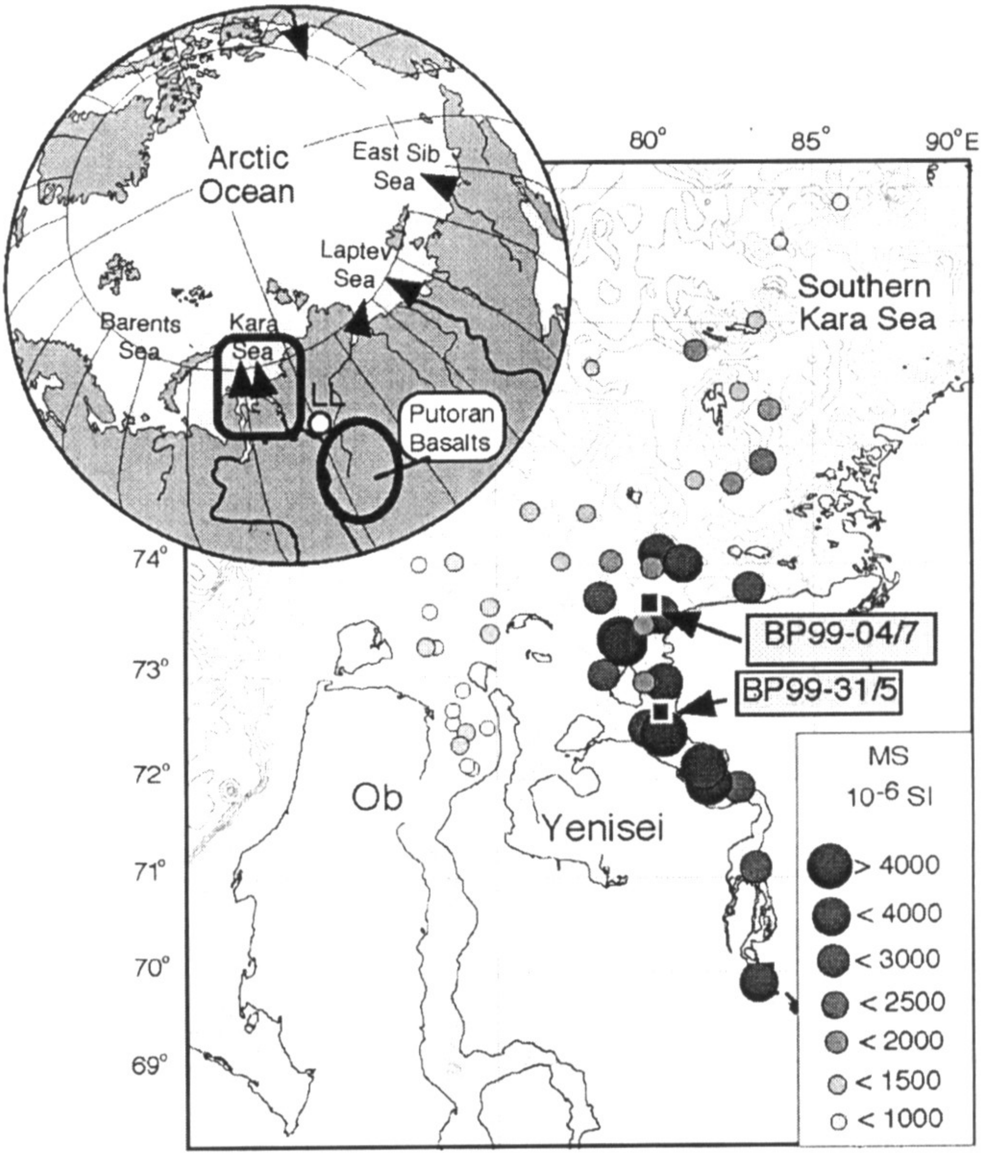


Figure 61 **Magnetic susceptibility (MS) values in the surface bottom sediments (Stein et al., 2004).**

4.4.6 TOC concentrations

TOC contents of surface sediments in the Ob and Yenisey Estuaries and in adjacent Kara Sea are shown in Fig.62 (Stein and Fahl, 2003). TOC values are the highest in the sediments of both estuaries (> 2%). The elevated TOC values were detected in some samples from the submarine channels to north of the Yenisey with fine pelitic sediments.

The terrigenous origin of organic carbon in the estuaries and in the southern Kara Sea is a well-known fact. In the MF's the most fine SPM trapped and accumulating. This leads to high TOC content in bottom sediments. Typical ratio C/N is in a range 9-14 and light δ^{13}Corg values of about -27‰ (Yenisey) and -28 to -28.7‰ (Ob) are clearly reflected this origin. Also support a terrigenous origin of organic carbon high concentrations of long-chain n-alkanes (C27 +C29 +C31) in surface sediments of the Ob and Yenisey transects (Fahl et al., 2003).

A general decrease in relative proportion of terrigenous organic carbon towards the north is quite obvious.

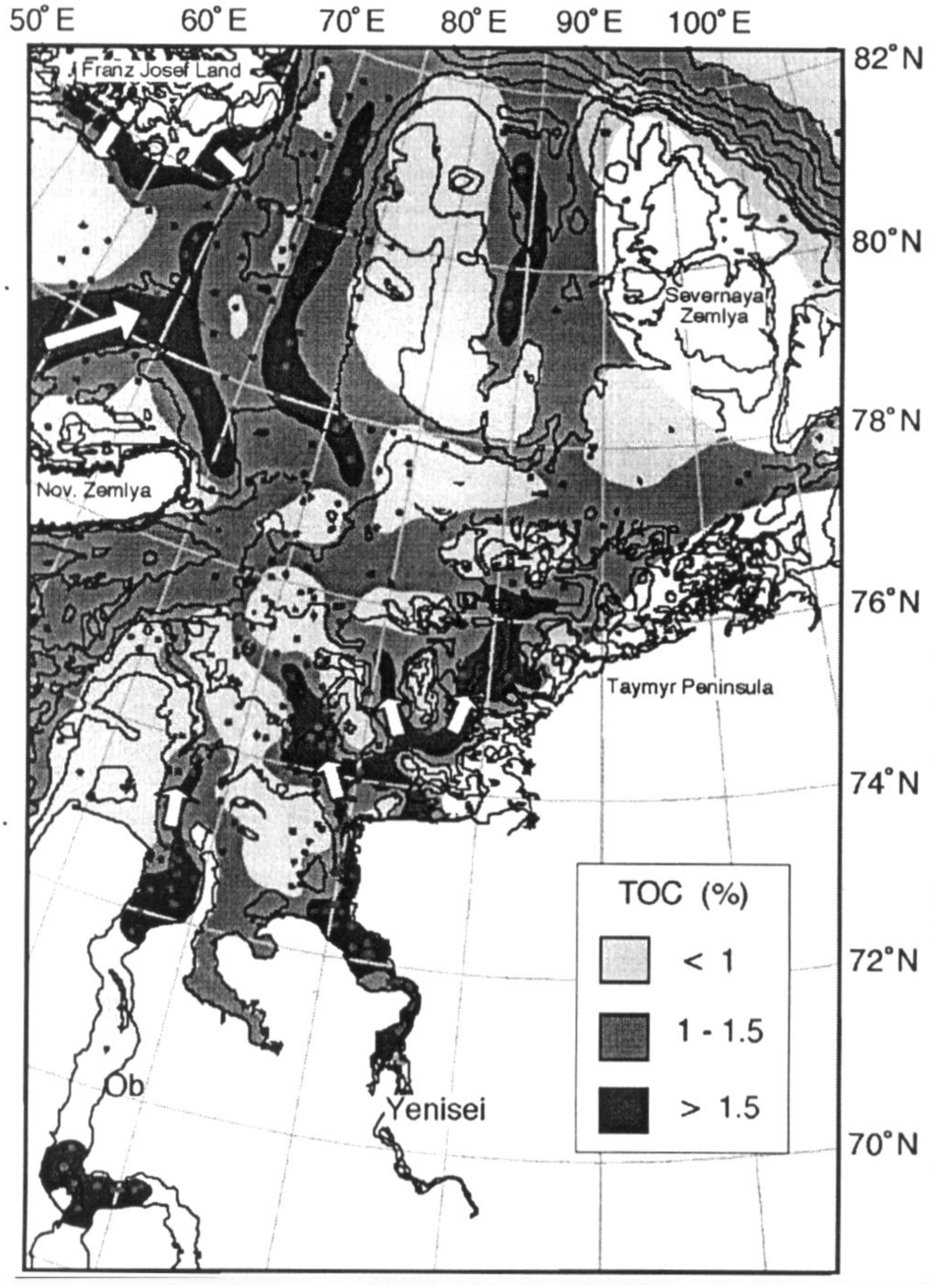


Figure 62 Distribution of TOC in the surface bottom sediments of the Kara sea. Open arrows indicate input and pathways of organic carbon (Stein et al., 2003).

4.4.7 Chemical composition

4.4.7.1 Major and trace elements in surface bottom sediments

During the last 10-15 years there were many geochemical studies of bottom sediments of the Obskaya Guba and the Yenisey Bay (Gurvich et al., 1994; Gordeev et al., 1995; Krasnyuk, 1998; Schoster, 1998; Miroshnikov and Asadulin, 1999; Krasnyuk and

Vanshtein, 1999; Schoster and Stein, 1999; Schoster et al., 2000, 2002; Sizov et al., 2001; Schoster and Beeskow, 2001; Levitan et al., 2002; Stepanets et al., 2002; Beeskow and Rachold, 2003; Stepanets et al.2004; Demina et al., 2006). These works show that the main features of elemental distribution can be attributed to the geology of the watersheds and the transport of sedimentary material by the Ob and Yenisey Rivers into their estuaries. Transport processes sort sediment by grain size and may influence sediment composition, since the composition of materials derived from various sediment sources can be modified by grain size sorting subsequent to discharge to the estuaries and on the shelf.

Very interesting paper (Viscosi-Shirley et al., 2003) related to clay mineralogy and multi-element chemistry of surface sediments on the Siberian-Arctic shelf from the Laptev Sea to the Chukchi Sea. To simplify interpretation of the multivariate chemical data set (Si, Al, K, Mg, Sr, La, Ce, Nd) the authors have looked for regional variability in sediment composition using scatter plots of single and multiple element ratios as suggested elsewhere (Boström et al., 1973; Heath and Dymond, 1977) and have used the factor analysis which provided an additional means of simplifying of geochemical data interpretation.

Siberian-shelf surface bottom sediment element data plotted as Si/Al vs. Mg/K and Si/Al vs. Sr indicate that there are four endmember compositions in the sediments. These are: 1) the shale endmember (Al, K, REE-rich sediments); 2) the basalt endmember (Mg-rich and smectite-rich); 3) the mature sandstone endmember (Si-rich); and 4) the immature sandstone endmember (Sr-rich). The factor analysis indicates that four factors are needed to account for most of variability in the elemental data that is the factor analysis confirms the presence of the four geochemical endmember compositions identified in scatter plots.

Krasnyuk and Vanshtein (1999), Miroshnikov and Asadulin (1999), Sizov et al., (2001) have found that the pattern of element distribution in the Ob Estuary bottom sediments was close to the normal distribution while in the Yenisey Estuary Fe, La, Ce, Th contents demonstrated clearly the bi-modal distribution. There are two maximum of Fe: the first is 4.27%, and the second- 6.64% Fe (Krasnyuk and Vanstein, 1999). The difference is statistically meaningful. All the elements determined were divided in two groups: with Fe> 5.84% (group 1) and with Fe< 5.84% (group 2). This difference is clearly visible in Fig.63. The correlation with Fe is very different in two groups. The group 1 includes Co, V, Ti, Ni, Cr, Rb, Mn, As, Br and Ba. The elements of this group have a positive correlation with Fe when Fe< 5.84%, and do not have any correlation when Fe>5.84%. The group 2 consists of Zn, Cu, Sr and Pb. Correlation with Fe is absent (or negative for Pb). And only Co has a positive correlation with Fe in full range of its content (it is an exception).

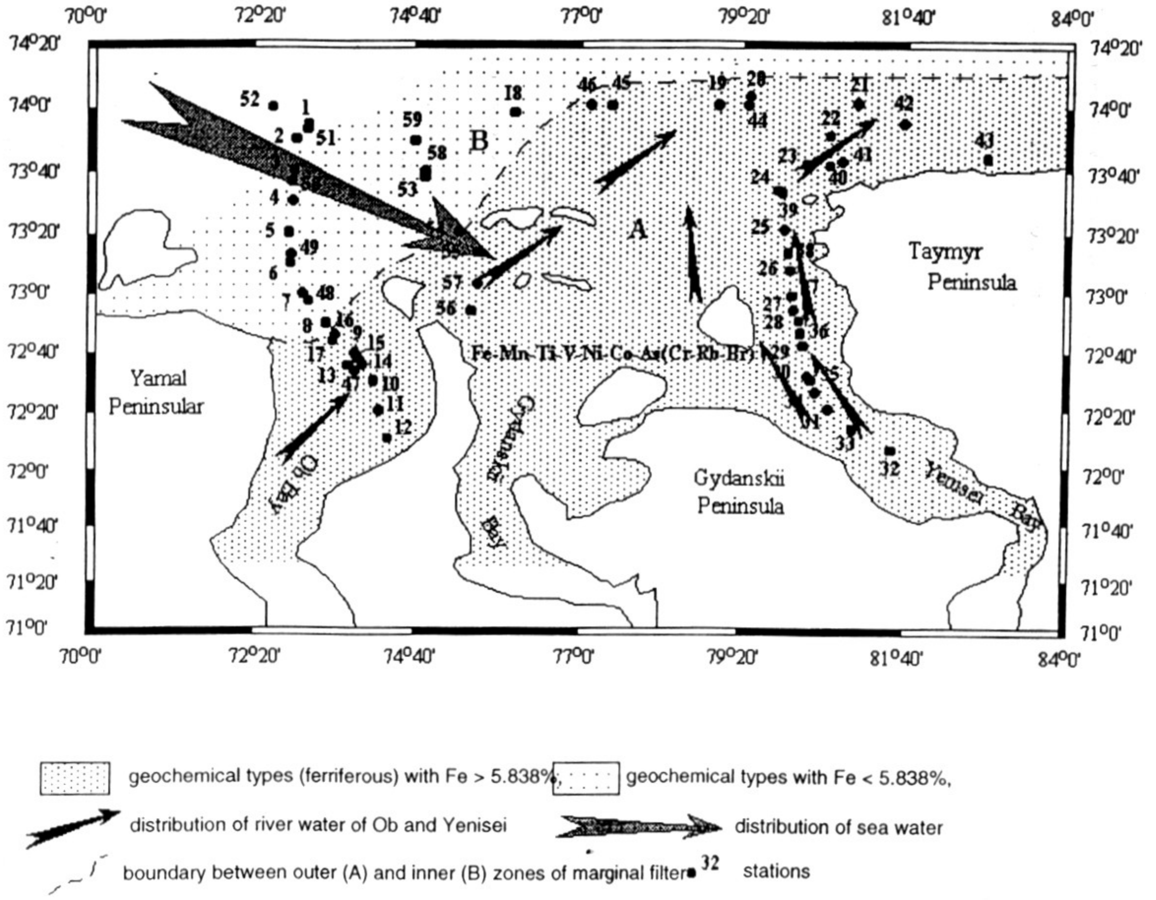


Figure 63 Distribution of geochemical types in the surface bottom sediments in the Ob and Yenisey Estuaries (Krasnuk and Vanshtein, 1999).

Two types of bottom sediments reflect, to author's opinion (Krasnyuk and Vanshtein, 1999), the different processes of their compositional formation.

The group 1 occupies the inner zone of the MF's. The mechanical differentiation of suspended sediment, as a main process in this area, is responsible for the absence of correlation with high Fe here. The elements of the group 2 are concentrated in the external part of the MF's, where the correlation with relatively low Fe is positive and they accumulated as a result of their sorption on Fe and Mn hydroxides from sea water.

So, the boundary between the areas of two groups localization in two estuaries reflect the transition between the inner (group 1) and external (group 2) MF's zones.

The Fe/Al ratio varies in a narrow range (0.7-0.9) but it is very indicative (Fig.64). In the Ob Estuary Fe/Al >0.89 near 72^{0}N, where the content of fraction $< 2\mu m$ is more than 50%. The main factor of control is salinity. It is a zone of intensive Fe and DOC flocculation. To the north the ratio is decreased but its value remains to be higher than in the shales (Schoster and Stein, 1999). In the Yenisey Estuary at 71-73^{0}N Fe/Al = 0.7-0.88. The step 3 of the MF's is located near 73^{0}N where water salinity is in a range 2-10-15‰. Fe in SPM is high here (Lukashin et al., 1999). Further to the north the ratio increases mainly due to occurrence of Fe-Mn nodules (Bogdanov et al., 1994).

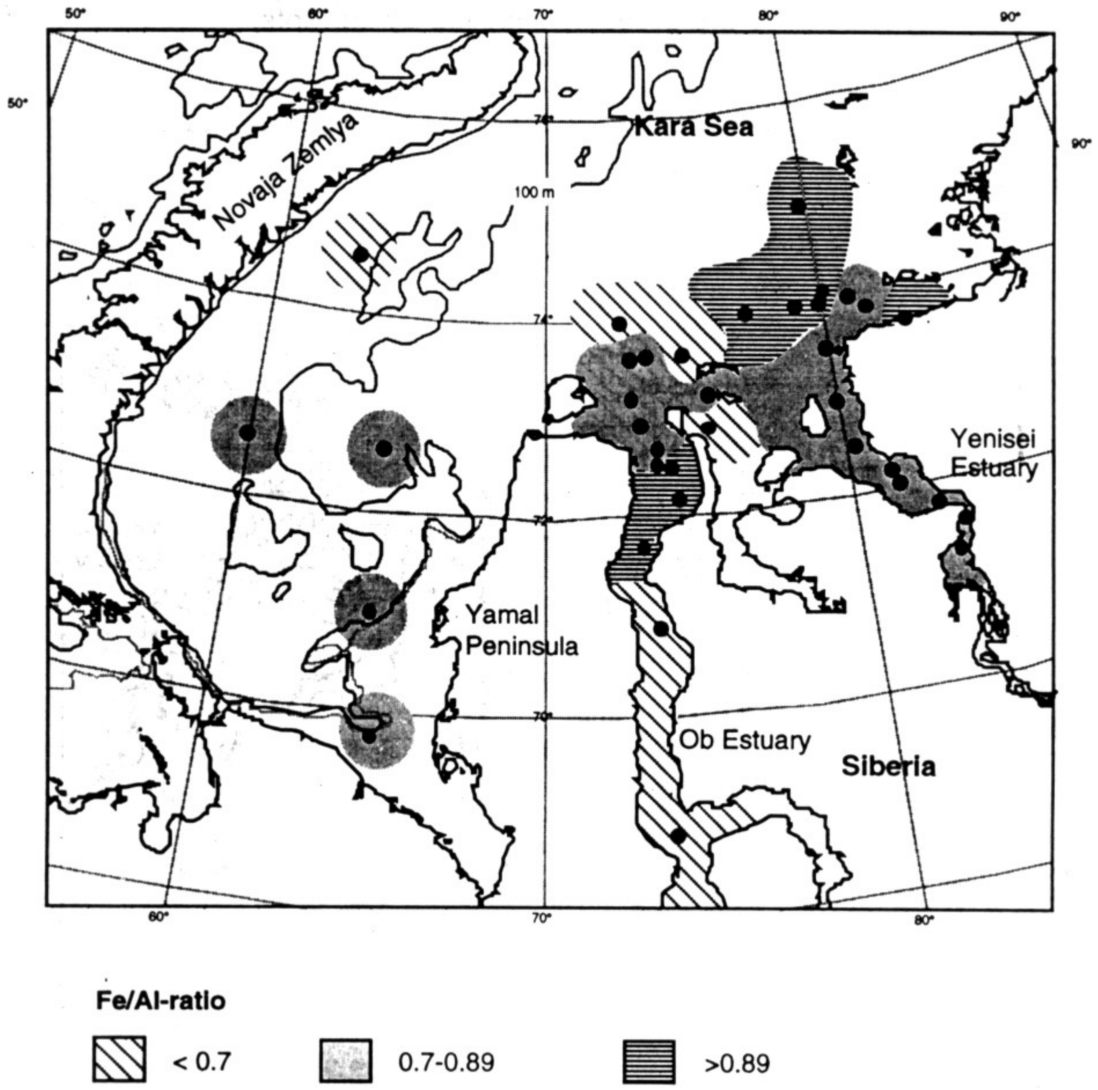


Figure 64 Distribution of Fe/Al-ratios in surface sediments of the Ob and Yenisey Estuaries and adjacent Kara Sea (Schoster and Stein, 1999).

It is interesting to know the distribution of labile and refractory forms of elements in surface bottom sediments along the transects from south to north in the Ob and Yenisey Estuaries (Fig.65 A and B, Demina et al., 2006). The chemical forms (or species) of metals (Fe, Mn, Cu, Zn, Ni, Co, Cr, Pb) were determined after successive chemical leaching of bottom sediment samples of natural moisture within 6 hours after collection on board of the R/V “Dmitry Mendeleev” (49-th cruise, 1993). The speciations of these forms were: 1) sorbed/carbonate-bound fraction (0.5 M acetic acid buffered by Na acetate, pH=4.8); 2) cations bound with Fe and Mn oxyhydroxides fraction leached by 1M hydroxylamine-hydrochloride buffered with 25% acetic acid- Chester reagent (Chester and Hughes, 1967); 3) the organic-associated fraction (30% H_2O_2 with HNO_3) (Kitano and Fujuoshi, 1980). These three fractions represent labile occurrence forms that are able to transform under environmental changes; 4) the refractory fraction is firmly fixed in the crystal lattice of minerals and unaffected by previous reagent attacks. It was calculated by difference between total content and sum of three labile fractions. The element concentrations were determined by AAS method in flame version (acetylene-air).

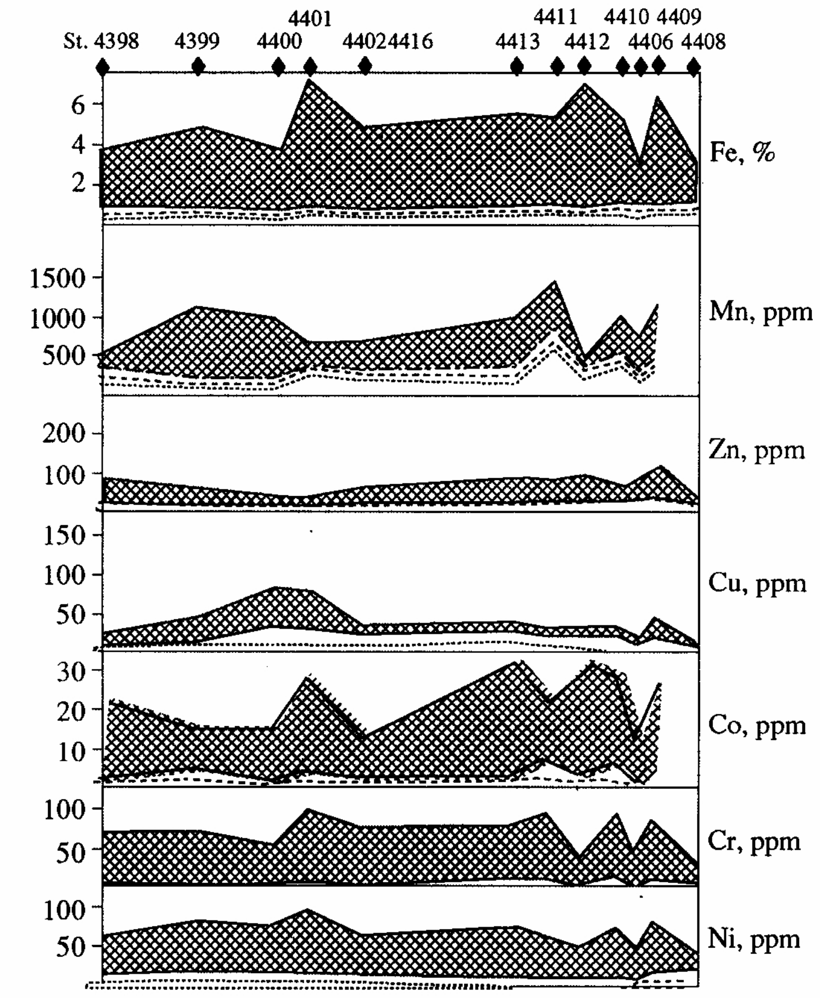


Figure 65A Bulk content and speciation of metals in the surface layer of sediments in the Ob section (DM-1993). Speciations of metals: 1- adsorbed + carbonate; 2- related to fresh Fe and Mn hydroxides; 3- organic + sulphides; 4- residual (lithogenic). (Demina et al., 2006).

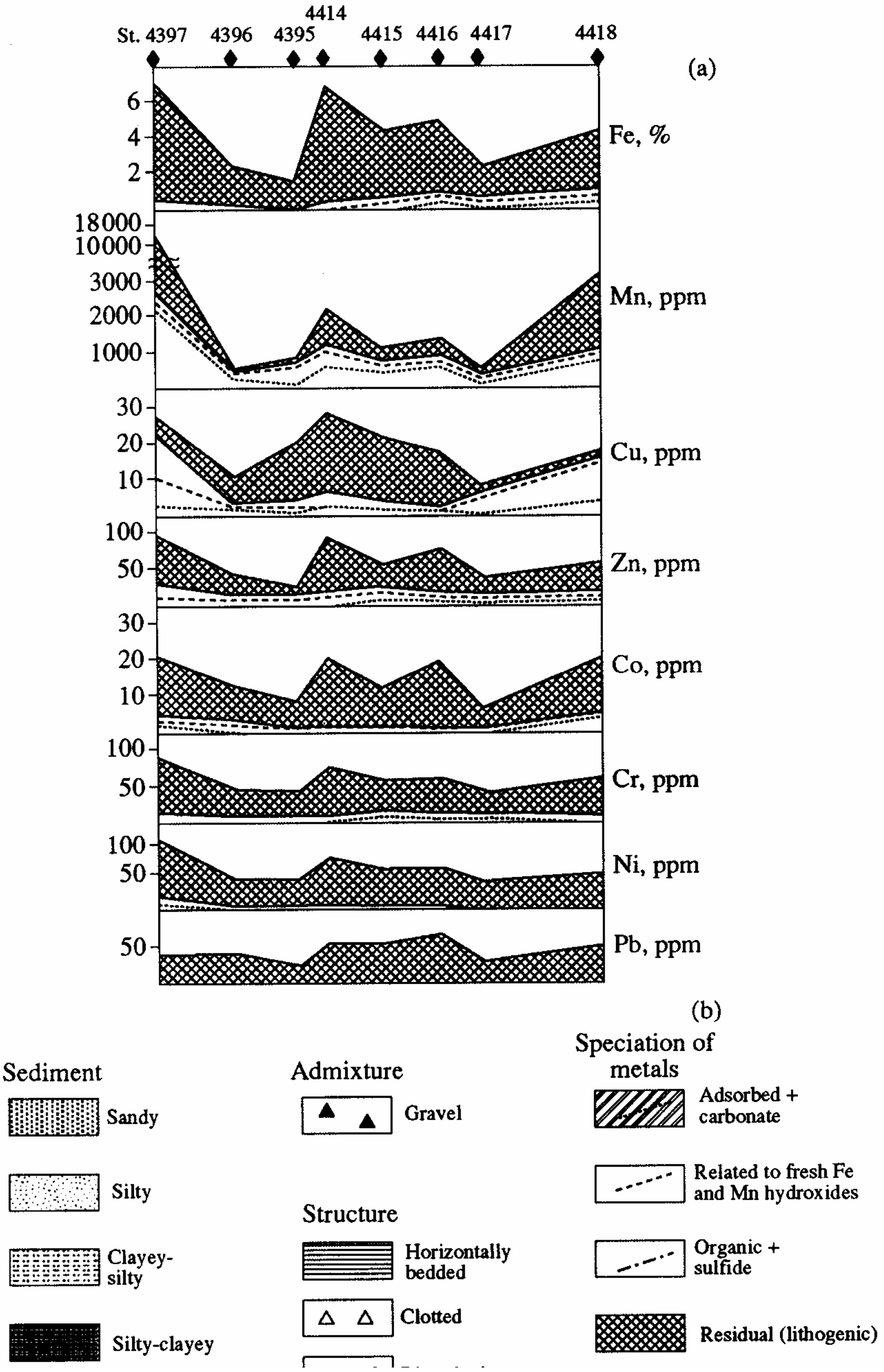


Figure 65B **Bulk content and speciation of metals in the surface layer of sediments in the Yenisey section (DM-1993). Speciations of metals: 1- adsorbed + carbonate; 2- related to fresh Fe and Mn hydroxides; 3- organic + sulphides; 4- residual (lithogenic). (Demina et al., 2006).**

The sediment samples of transects accord to the first three facial environments (A, B and C) (Levitan et al., 2005 – see section 4.4.1). In the river facie (A) the sediments vary from gravel-sandy deposits to silty-pelitic muds. The refractory fraction dominates in the southern parts of estuaries contained approximately 70 -95% of Fe, Co, Cr, Pb and Ni and about 50% or less of Mn and Zn. And only for Cu this fraction is of minor significance: only 31% of Cu in average is in refractory fraction, the larger Cu part is in geochemically labile fractions.

In the facial environment (B) (Sts. 4416 -4414, Ob Estuary, and Sts. 4411 -4402, Yenisey Estuary) we see the highest content of mobile forms of Fe (in the Ob Estuary) and especially of Mn and associated trace metals. These are the physico-chemical parts of MF's of the estuaries (so-called colloidal pump –C-pump). Massive flocculation of dissolved C_{org} and Fe and Mn take place that increases the ratio Fe/Al and a portion of labile forms of elements here. In the northern part of the transects a sum of labile forms of Mn and Cu, Zn, Ni and Co , as the authors note, increase in accordance with the finer grain- size composition of sediments.

So, geochemically inert (lithogenic or clastic) modes of the studied elements dominate in bottom sediments of both estuaries. It is reasonable to conclude that lithogenic processes play a crucial role in the accumulation of the metals in sediments. Shallow depth and low temperature of near bottom waters do not promote substantial transformation of metal species in riverine SPM supplied to the estuaries and sea basin (Demina et al., 2006).

Stepanets and co-authors (2002, 2004) have considered the chemical composition of the Ob and Yenisey Estuaries bottom sediments from a point of view of their contamination by selected heavy metals. They noted that the lateral distribution of Pb, Cu and some other elements was different from Fe distribution. The authors suggested that irregular distribution of Cu and Pb might be related to the influence of source- works of mining plants in Norilsk. This suggestion may not be rejected but, to our opinion, this needs in much more comprehensive confirmations.

4.4.7.2 Chemical elements in grain-size spectrum (except REE)

In previous sections we mentioned repeatedly about close correlation between distribution of chemical elements in bottom sediments and their grain size. We have a possibility to demonstrate the regularities of major and trace element distribution in granulometric spectrum of bottom sediments. Major and trace element contents in grain-size fractions obtained by the method of elutriation (see Section 3.1) were measured in four samples of bottom sediments. The samples were selected to characterize the river and open sea end members of two transects.

Fig.66 shows the distribution of Si, Ca, Fe, Cu, Pb and Ni in size fractions of bottom sediment samples on stations 4409 and 4399 of the Yenisey transect. The results are very similar for both stations. It is distinctly visible that Si and Ca are decreasing monotonously from the coarser to finer fractions (Ca in fr.> 4µm at station 4409 is considered as a discard), while Fe, Cu, Pb and Ni, on the contrary, are increasing in the same direction. The ratio Mefr.>50µm/ Mefr.< 4µm may serve as a measure of contrast in grain-size spectrum. The values of these ratios are given in Table 37. All the elements are divided in three groups:

1) Si, Hf, Ca (Ca in the Yenisey sediments) – concentrated in the coarser fractions;

2) Na, K, Ca (Ca in the Ob sediments)- monotonous distribution;
3) TOC, Al, Fe, Mg, Mn, Cu, Pb, Ni, Co, Cr, Rb, Cs, Sc, Th – concentrated in the finer fractions.

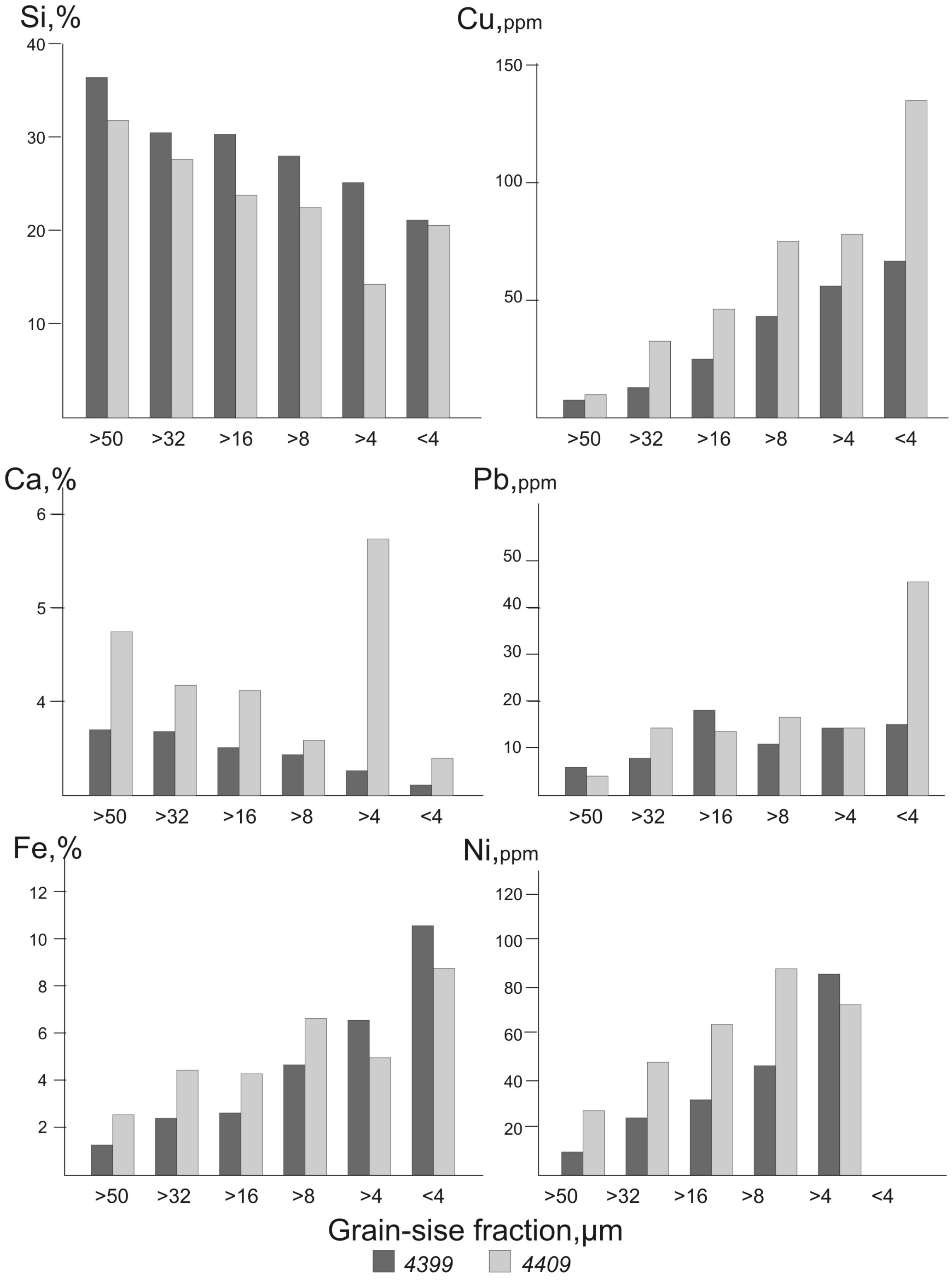


Figure 66 Distribution of Si, Ca, Fe, Cu, Pb and Ni in size – fractions of bottom sediment samples on Sts. 4409 and 4399 of the Yenisey transect (DM-1993).

This dividing of elements is quite regular. Si, an element of group 1, is concentrated in coarse fraction due to domination of quartz which is a diluter for all other elements (Gurvich et al., 1994). The coefficient of contrast for Si is not high -1.5-1.7 because fine fractions contain Si in clay minerals and fine quartz fragments. Ca, as well as Si, is abundant in fr.> 50µm in the Yenisey sediments (Ca content – 0.9-2.8%) while in the Ob sediments (Ca content – 0.54-0.76%) this metal is distributed monotonously in different fractions. The clay minerals do not contain much Ca, particularly kaolinite, illite and chlorite. Sum of these clay minerals in fraction < 1 µm at St. 4409 is 20% less than in the Ob sediments (Gorbunova, 1996).

Calcite is chaotically distributed in size fractions. Indeed, carbonate shells and their fragments play an important role in Ca distribution in sediments. But the sediments of both estuaries and the Kara Sea contain a low $CaCO_3$ (normally < 2%) (Gurvich et al, 1994).

Majority of elements (group 3) is distributed in grain-size spectrum in contrast to Si and Ca that means they are concentrated in the finest fractions. This result is quite natural and is explained by change of mineral composition from predominantly quartz and, in lesser degree, feldspars in coarser fractions to clay minerals in pelitic fractions.

Concerning Hf distribution we may do a reference to the work (Gurvich et al., 1980) where it was shown that Hf as an element of the accessory minerals was contained in higher quantities in coarser fractions of near shore terrigenous sediments of the Pacific Ocean. Hf was concentrated in shallow sediments near the shores and indicated a tendency to reduce its concentration in terrigenous sediments with depth. It is probably this regularity in Hf behaviour in coastal sediments appear in suspended matter of transit zone river/sea. This was confirmed by Hf behaviour in the Ob and Yenisey SPM (see Section 4.2.2.7).

4.4.7.3 REE in grain-size fractions of bottom sediments

Fluctuations of the coefficient of contrast for REE in bottom sediments of the Ob and Yenisey Estuaries (Fig.34) are rather small (if to compare to SPM samples) despite of their very diverse granulometric composition. Another behaviour was found for St.4399 (the Yenisey transect, Fig.7). Here light and middle REE (La, Ce, Nd, Sm) are associated with fine fractions (K=0.2-0.6), Eu shows a splash and further beginning from Gd the coefficient rises from 0.7 to 1.8 for Lu. In other words, from Gd to Yb and Lu occurs the alteration of element's association from fine fractions to coarse fractions, starts from Eu. How to explain the concentration of middle and heavy REE in coarse fraction of bottom sediments at station 4399?

The mineral composition of bottom sediments of the Kara Sea reveals the following (Gorbunova, 1996; Serova and Gorbunova, 1998):

- No significant difference in clay mineral composition of the finest fraction (<0.001mm);
- No difference in quartz and feldspars in fraction < 0.01mm;

- 3-4 times more of black ore minerals (mainly magnetite and ilmenite) and 2 times less of clinopyroxene in heavy sub-fraction of the fraction 0.05-0.1 mm in the Ob bottom sediments.

Dark-coloured minerals as it is known contain majority of middle and HREE as well as pyroxenes (Balashov, 1976). But black ore minerals compose insignificant part of heavy sub-fraction (<10%), at that time clinopyroxene makes up its main part- 23-35% in the Ob sediments and 57-70% in the Yenisey sediments (heavy sub-fraction is 6.5% at station 4399 and much lower at stations 4417 and 4397- 2.7-3.8%). Probably, at least partly, it explains a concentration of HREE in fraction >50(m at station 4399.

It was noticed that Fe-Mn hydroxides were most abundant in sediments of station 4397. Similarity in distribution of REE in size fractions of this station and station 4417 with minimal role of hydroxides indicates a low effect of hydroxides in this process. We can say probably the same on the role of organic matter because its content in sediments of station 4399 (0.84%) and station 4397 (1.09%) is very close. It is interesting to note that Eu, as well as HREE, is concentrated in coarse fraction of station 4399 but it is not a case for the Ob sediments.

The average shale normalized REE patterns (the average shale composition taken from Sholkovitz (1988)) in granulometric fractions of bottom sediments in both estuaries are similar to that of SPM (Fig.32). No real enrichment of LREE relatively to HREE exists. One can note more compact distribution of REE patterns in fine and coarse fractions and definite positive Eu-anomaly (+1.3 to +2.4). There are at least two reasons to explain this Eu-anomaly. First, the bottom sediments of both estuaries (light sub-fraction of size fraction 0.05-0.1 mm) contain significant quantities of plagioclase (Levitan et al., 1996) which concentrates Europium (Eu/Sm=0.2-0.3 in typical shales and >2 in plagioclase) (Balashov, 1976). Sediments of station 4397 contain 1.5 times more plagioclase than sediments of station 4399, and Eu-anomaly is more expressed at the first station. Second, Goldshtein and Jacobsen (1988) have shown that the REE patterns of river suspended load are sensitive to the drainage basin geology. In the Yenisey basin the Siberian trap basalts are spread, fractionated material of which displays a positive Eu-anomaly.

5 Comparable geochemistry of the Ob and Yenisey Estuaries

As it was declared in the introduction, the main aim of the work is to compare the geochemical characteristics of water, SPM and surface bottom sediments of the lower courses and the estuaries of the two biggest Arctic rivers - Ob and Yenisey. To achieve this, the results of a whole series of Russian and Russian-German expeditions from 1993 to 2003 to the Kara Sea and the Ob and Yenisey Estuaries has been used. The extensive data set is a good base to study the influence of seasonal and inter-annual variations of meteorological conditions to the catchment area and hence the changes in river water and SPM discharge into the Kara Sea

The variations have a strong impact to geochemical and biogeochemical processes in the estuaries and adjacent sea. Due to the large data base it is possible to compare the behaviour of chemical elements and components in different years which makes the final conclusion more reliable. Practically all expeditions have been carried out in August and September (see Section 3 and Table 38) which makes a comparison of the data of these expeditions almost without any stipulations possible. However, on the other hand, data on winter and spring flooding are lacking. In the previous sections data obtained in recent expeditions. The authors of the book tried to realize a unified approach to the results of different expeditions have been presented to a large extent and a unified approach of the results have been made. The work of the MF's of the two Siberian rivers in different years was considered (MF model is presented in section 4.3.1) and numerous dependencies of element concentrations, components and hydrochemical parameters on salinity have been shown. Inclusion of so many figures with such type of dependencies can be explained by an aspiration to provide the most full picture (at this more than half of these new figures appeared to be out of the frames of the book).

The following conclusions are based on the comparison of all parameters, characteristics and processes considered along with distinguishing of resemblances and especially differences between two huge estuaries.

5.1 The used materials

The data used in this work have been obtained in the Russian and Russian-German expeditions from 1993 to 2003 (Table 38). The materials of the BP-2002 expedition were touched very superficially because there were only few stations in the Ob Estuary that did not allow creating the reliable dependencies of components and salinity.

The table shows that the transects in a full range of salinity were not in all expeditions obtained, and that the data on the Yenisey Estuary appeared to be more representative than these of the Ob Estuary.

5.2 Geological differences between the two river catchments areas

The geology and climate of the Ob and Yenisey catchment areas are presented in section 2.1. The geological differences of the areas have a strong influence to the geochemistry of water, SPM and bottom sediments of the estuaries. The catchment areas of both rivers include the Siberian Lowland which supplies the rivers with the weathered material of shales type. The main distinguishing geological features are the Triassic plateau basalts and the tuff deposits of the Putorane Massif in the Yenisey catchment area (Fig.1). The Nizhnyaya Tunguska and the Podkamennaya Tunguska drain this area and deliver about 70% of the modern annual Yenisey discharge (Meade et al., 2000). Therefore, the Putorane plateau can be seen as the most important source to the Yenisey Estuary, whereas the Ob is feed largely by material from the Siberian lowland.

5.3 Physico-geographical characteristics of the rivers and their estuarine-deltaic areas

The estuarine-deltaic areas of Ob and Yenisey have similar origin. The postglacial transgression of the World Ocean resulted in flooding of the erosion river planes formed in conditions of the sea regression. As a result, the ingression bays (Ob Guba, Taz Guba, Yenisey Bay and other) were formed with the deltas at the tops of these bays.

The main characteristics of the systems are given in Table 39. The rivers have practically similar catchment areas but differ in their specific water discharge (Yenisey is 1.5 times higher) and specific sediment discharge (Yenisey SPM load is 3.4 times less). Both rivers have a lower specific water and particularly specific SPM discharge in comparison to the global average (11 l/sec. km^2 and 185 t/km^2, respectively). The reasons for the low SPM load in Arctic rivers are low thickness of the weathering crust in the catchment area, widespread permafrost and negative temperatures for the most part of a year, low precipitation, the plane tundra relief with a dominance of broad swampy lowlands and numerous lakes, and low human activity (Lisitzin, 1994; Bobrovitskaya et al., 2003; Gordeev, 2006).

A new stochastic sediment transport model (Morehead et al., 2003) makes an attempt to explain why arctic rivers have a low sediment load when compared with the global average. Because it is sensitive to drainage basin temperature, the model is used to estimate the impact of a climate-warming scenario on the loads of high-latitude rivers. A 30% increase in the flux carried is estimated for every 2^{0}C of warming and 10% increase for every 20% increase of discharge. Peterson et al. (2002) consider that the discharge of six largest Eurasian rivers (Yenisey, Lena, Ob, Pechora, Kolyma and Severnaya Dvina) would increase by 18-70% by 2100 due to an increase in the global surface air temperature between 1.4 and 5.8^{0}C by 2100 (IPCC, 2001). It means, that the sediment flux of the six arctic rivers would increase from 30 to 122% by 2100 (Gordeev, 2006).

The Ob Guba is 2 times longer, 2-3 times wider than the Yenisey Bay, and its total area is more than 2 times larger than the Yenisey delta-estuarine area. At the same time the typical water currents in the Ob Guba are lower than in the Yenisey Bay. That is important for the biogeochemical and sedimentological processes in the estuaries.

5.4 Inter-annual and seasonal variations of river water and SPM discharges

All processes in the estuaries, including geochemical and biogeochemical ones, take place under significant impact of water and sediment discharges and their inter-annual and seasonal variations. Therefore it is important to know these variations.

In section 4.1 it was shown that inter-annual variations of the average run-off of the Ob River were more than 20% between 1938 and 1996, and an increase at the lower course (Salekhard) of about 5% takes place. The specific discharge changed from 3 l/sec. km^2 in 1969 to 6.3 l/sec. km^2 in 1979(Fig.19 B). Multi-annual variations of sediment flux were also very significant. The annual specific flux of sediments changed from3.6 t/km^2.yr in 1968 to maximum of 8.8 t/km^2.yr in 1971. However, the sediment flux in the Ob River at Salekhard shows no statistically significant trend despite to a significant impact of human activity in the upper basin. The main reason, as it was mentioned above (section 4.1,a), is the huge flood plane between Belogorie and Salekhard that acts as a very effective sediment trap.

The multi-annual variations of water and sediment discharges in the Yenisey (Fig.16 and 17) are, based on analyses by Bobrovitskaya et al (2003), insignificant with an increase of 6% in water discharge during the period from 30-th to 90-th of the last century. The annual sediment flux, on the other hand, decreased 2.8 times due to the great influence of the dam constructions.

The seasonal variations during the time of the expeditions BP-1997, BP-1999 and BP-2000 may be seen in Fig. 72 (see below). There is a pronounced discharge pick in spring and relatively low water flow between September and April. Differences in discharge in the second half of August-September between three years are observed. The highest discharge occurs in the Ob River (Salekhard) in 1999 and comparable discharges in 1997 and 2000. In the Yenisey River (Igarka) the discharge was highest in 1997 and equal fluxes occurred in 1997 and 2000.

5.5 The chemical composition of river water

Major ions

The concentrations of major cations and anions in the lower course of Ob and Yenisey water are similar to global averages (Table 1, Fig.67). At the same time, the Yenisey water is somewhat closer to the global concentration of almost of all major ions, and its multi-annual mineralization is also closer to the global one (107 mg/l – Yenisey, 121 mg/l- Ob, 99.7 mg/l- global (Meybeck, 1979)). The major ions and mineralization are not stable in both rivers during a year. It was shown clearly on the Lena River that during the year not only the concentration of major elements and total mineralization change, but also the hydrochemical type of water (Fig.19). Unfortunately, we do not have such type of data for the Ob and Yenisey Rivers.

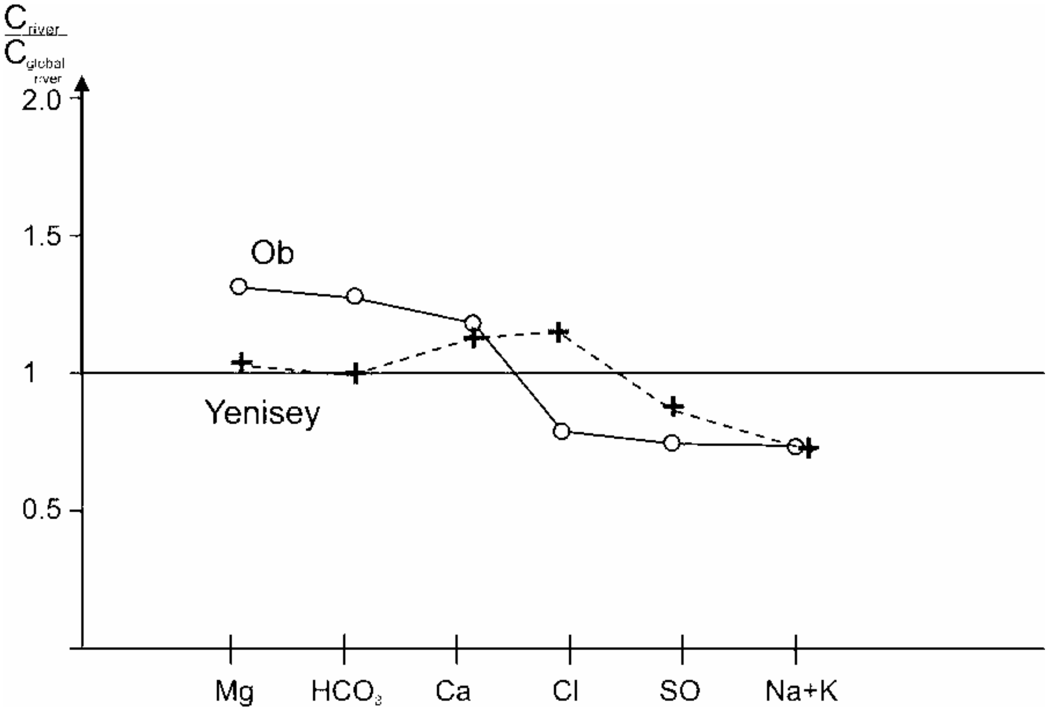


Figure 67 **Comparison of dissolved major anions and anions in the Ob and Yenisey Rivers.**

The hydrocarbonate water type with Ca+Mg dominating over Na+K (this ratio is 3.74 in Ob and 3.25 in Yenisey, 2.13 in global average) is typical for both rivers and indicate carbonate weathering in both catchment areas.

So, two rivers are practically identical on the major ion composition, and this factor may not result to any significant differences in the estuarine geochemistry of two rivers.

DOC

The data on DOC concentrations in Ob and Yenisey are limited (Table 2). The data show DOC of 7-10 mg/l in the Ob and 4-8.5 mg/l in the Yenisey (in average 7.7 and 8.2 mg/l respectively). Based on these data no significant differences in DOC concentrations of both rivers can be revealed, except that DOC in these rivers is about 1.5 times higher than the global value.

Nutrients

The content of dissolved inorganic nitrogen and DON in both rivers is lower, and that of phosphates higher than the global average (Table 3). The data on dissolved silica from different authors are difficult to compare. Whilst data of Tzirkunov et al. (1998) and GEMS (1995) have the same source (the Roshydromet data for 1980-1990), data of Gordeev et al.(1996) are mainly taken from the Tiksi Regional Department of Roshydromet for period 1985-1995. The latter reveals that Si concentrations in the Ob and Yenisey are lower than global level. This is expected because of the dominant carbonate weathering in the catchment area of two rivers.

The Ob River water appears to be enriched in N-NO_3, SiO_2 and P-PO_4. This is an important fact, as phosphate and nitrate may be the limiting factor for phytoplankton development in the estuaries.

Trace elements

Our new assessments of the average dissolved trace metals in the lower courses of the Ob and Yenisey Rivers are presented in Table 8. These assessments are compared to the global averages from Martin and Gordeev (1986) with corrections and also to the recent publication of Gaillardet et al (2004). The authors of the latter use published results since the early 1990-s. Here, unpolluted river water samples were measured after filtration (0.2-0.45µm filters). The analyses have been done by inductively coupled plasma mass spectrometry (ICP-MS). The review of these data reveals that the variability of trace element concentrations in river water through time was very high. Asian rivers, however, have received relatively little attention compared to rivers of North and South America and Africa.

A comparison of trace element concentrations in the Ob and Yenisey with global assessments show that the Ob water in its lower course is characterized by slightly higher Fe, Cu and Ni, but practically equal concentrations of Sr and Mn, and lower Zn, Cr, Pb and Cd. The water of the Yenisey is enriched in Zn and Sr, contains equal Fe, Cu and Ni, and lower concentrations of Pb and Cd.

It is necessary to note that, firstly, the question is about the river water just near the river deltas but not about the upper river basins where trace element concentrations may be much higher (see section 4.2.1.4). And secondly, taking into account the work of Gaillardet et al.(2004) and only little difference in trace elements in the two rivers ,it is possible to speak about similarity between two Siberian rivers and the global rivers in their trace element concentrations. A comparison between the Ob and Yenisey (Fig. 68) demonstrates that the Ob River water is enriched in Ni, Pb, Fe, Cd, Hg and Cu, and only Sr and Zn concentrations are higher in the Yenisey River water.

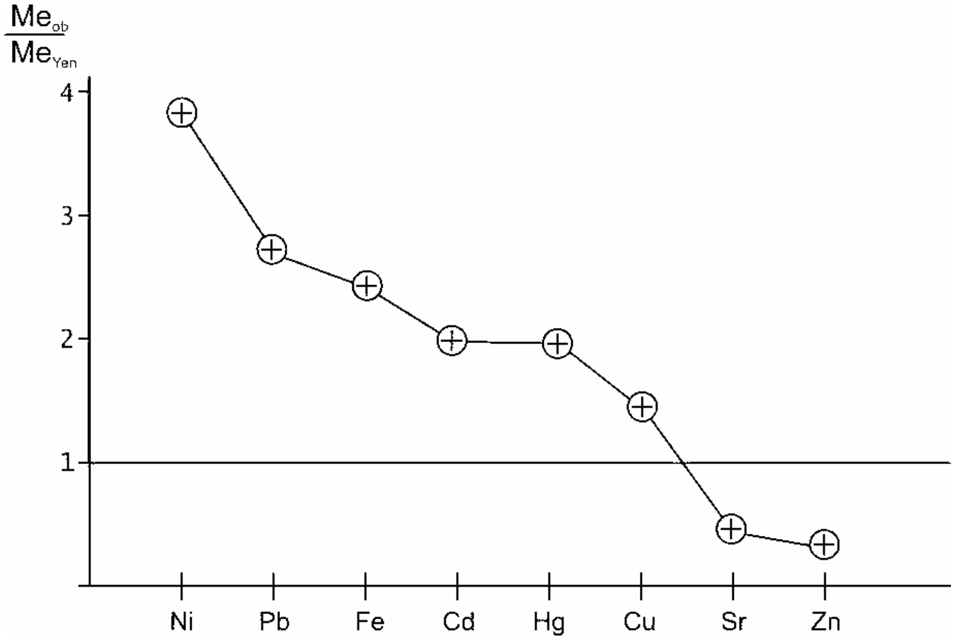


Figure 68 Comparison of dissolved trace elements in the Ob and Yenisey Rivers.

5.6 Chemical and mineralogical composition of river SPM

SPM

Very low concentrations of SPM are typical for the Ob and Yenisey Rivers, the main reasons of what were discussed in Section 5.4. The SPM concentration in the Ob River is higher than in the Yenisey. Dam constructions in the upper and middle Yenisey basin during the middle of the last century have caused the decrease in SPM concentrations and the fluxes compared to its natural level.

Grain-size distribution

Granulometric composition of SPM of both rivers is similar with a gradual decrease from the finest particles to coarse ones and a small peak in the range of 30-50 μm (Fig.30).

Clay mineralogy

Clay mineral composition of SPM is also very similar in both rivers. Smectite and illite prevail, whereas kaolinite and chlorite play a subordinate role (Table 11).

POC

Data on POC in SPM of the rivers are very scarce (Table 12) Therefore it is difficult to compare POC content. POC determinations in SPM samples of the expedition DM-1993 show that the Yenisey SPM is richer in organic carbon (4.7%) compared to the Ob SPM (2.9%). However, the more comprehensive study of POC in the Arctic rivers is needed.

The SPM of the three largest Arctic rivers – Ob, Yenisey and Lena is significantly enriched in organic carbon in comparison to its global average (1%). This fact is in good agreement with the proposed negative correlation between POC and SPM concentration in the World rivers by Meybeck (1982).

Nutrients

The data on particulate phosphorus (PPh) and particulate nitrogen (PN) (Section 4.2.2.6) show that PPh content in Ob SPM is 0.41% (0.04 mg/l) and 0.30% (0.011 mg/l) in Yenisey SPM. The calculations assess the organic part of total PPh to be about 40% in both rivers. PN in Ob SPM is 0.90% (0.09 mg/l) and in Yenisey SPM 1.32% (0.05 mg/l).

Chemical composition

The available data on chemical composition of SPM of the Ob and Yenisey were considered regarding their possible sources. The El/Al ratio for selected major and minor elements and Mg/K ratio, as the most sensitive proxy of basalt origin, are given in Table 43. The same ratios of typical Siberian trap basalts and average shales have been included for comparison. The ratios for basalts and shales show the most significant differences in Mg/K, Mg/Al, K/Al, Ca/Al ratios for major elements and in Ni/Al, Cr/Al, Rb/Al, V/Al and Zr/Al for trace elements.

The Mg/K ratio in Yenisey SPM is twice the value of Ob SPM. In Ob SPM the ratio is comparable with shale, while in Yenisey SPM it is even lower than that of Siberian basalts. Nevertheless, the values show the strong influence of Siberian basalts on chemical composition of Yenisey. Mg/Al and Ca/Al are higher and K/Al is much lower in basalts compared to shales. The ratios of Si, Fe and Ti to Al in SPM do not differ significantly as well as they do between basalts and shales.

Among trace elements the ratios Ni/Al, Cr/Al and V/Al are higher in Yenisey SPM in accordance with the previous conclusion. Rb/Al in basalts is 30 times less than in shales but data on Rb content do not exist.

In the work (of Viscosy-Shirley et al., (2003) it was shown that the shelf bottom sediments in the eastern Arctic Seas, for which the end member is shale, have a high content of Ce, La and Nd and total sum of REE. The determinations of Ob and Yenisey SPM (49-th cruise of R/V "Dmitry Mendeleev", 1993) show that the Ce content as well as La and Nd are about two times higher in Ob SPM in comparison to Yenisey SPM. So, the data presented show obviously that the main source of SPM in the Ob River originate from the Quaternary deposits on the West Siberian Lowland with a composition similar to shales. The behaviour of particulate chemical elements in the estuaries is largely conditioned by the level of phytoplankton activity. The metals, and trace elements, are involved into the biocycles and significantly change their initial concentrations. For major elements such as Na, Mg, Ca, K exchange reactions on suspended particles may take place.

A comparison of elemental composition of SPM between Ob and Yenisey is given in Fig. 69.

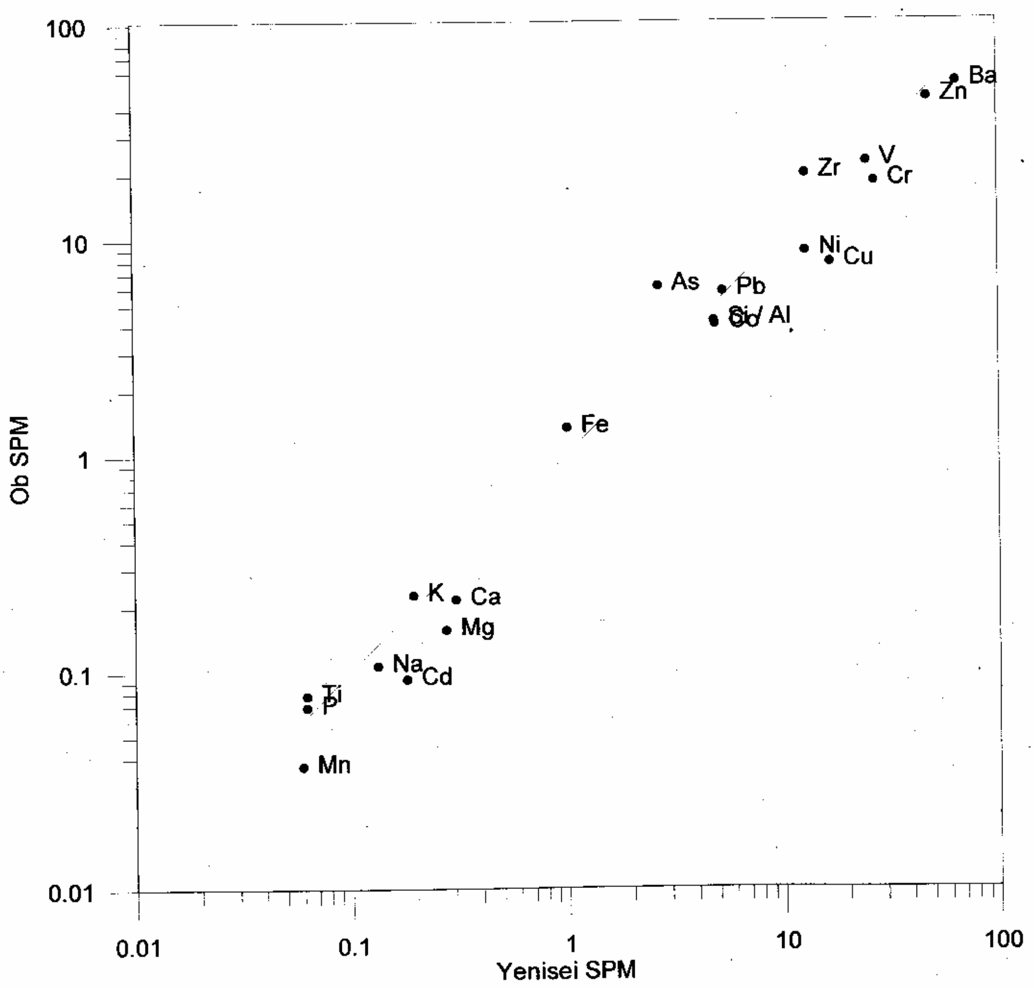


Figure 69 Comparison of mean element El/Al-ratios in the Ob and Yenisey SPM.

5.7 Estuarine processes

The estuarine zone (the marginal filter) is very important area for geochemical cycling of chemical elements (Section 4.3.1). It is a great system in which massive transfer of fluvial sedimentary material to the bottom sediments is the general direction of the process. It is an area of dramatic change of terrestrial geochemistry to marine geochemistry.

5.7.1 Hydrology

The historical data show a permanently existing pycnocline in the estuaries of both rivers. However, recent instrumental measurements of salinity and temperature revealed extremely strong gradients up to 5-10‰/10 cm and 1.5-2.^{0}C/10cm (Harms et al., 2003).

The difference between the hydrological regimes in the estuaries is quite apparent. The frontal zones in the Ob Estuary are not as sharp as in the Yenisey Estuary (Fig. 4 and 6).

The difference between surface and bottom water salinity is more pronounced in the Yenisey Estuary (up to 20‰). The penetration of saline waters into the Yenisey Estuary occurs quite frequently while in the Ob Estuary it is almost absent and the haline structure is weaker. At the same parallels salinity of waters in the Ob Estuary is approximately 5‰ lower than in the Yenisey Estuary (Burenkov and Vasilkov, 1994).

Model constructions reveal that in the beginning of August an intense NW flow in the estuaries drive the surface freshwater plume into the central Kara Sea. At the bottom, however, the extent of freshwater plume is much smaller. There exists a SW flow along the Taymyr coast which is stronger than the corresponding surface flow. A bottom counter current compensates this strong off-shore flow at the surface (Fig.70). Harms et al., (2003) assume that this flow brings at summer time saline water from the NE Kara Sea towards estuary, forming a pool of saline bottom water in front of the river mouth. This pool may be a source of saline water even in the river delta.

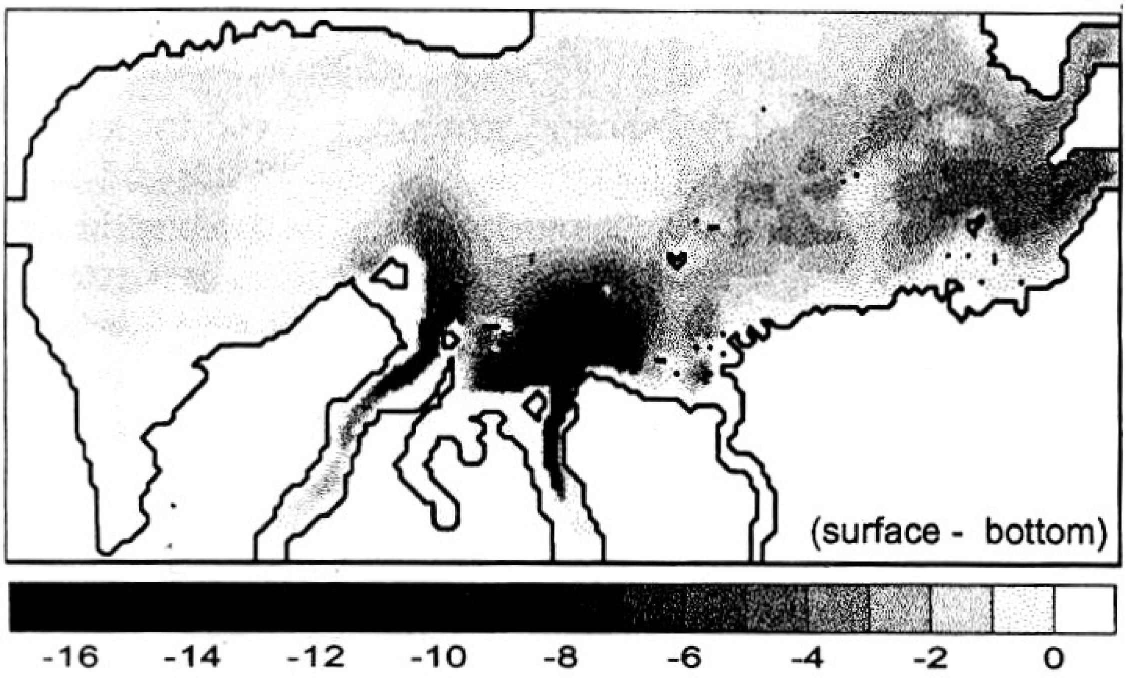


Figure 70 Simulated salinity difference (surface-bottom) at the 5-th of August, climatological year (Harmes et al., 2003).

The model results suggest a more pronounced salt intrusion in the Yenisey than in the Ob Estuary as a result of the tidal mixing which is weaker in the Yenisey Estuary due to higher tides in the Ob Estuary. Another important feature is a shape of the sea bed of the estuary: deeper and narrower in the Yenisey and broader and shallower in the Ob. The third point is the geographical orientation of the estuary. The prevailing NE wind directions in summer result in a maximum off-shore transport of fresh water while the orientation of the Ob Estuary is different and the SE winds required for a maximum influence are less frequent (Harms et al., 2003). In winter, cyclonic vorticity prevails over the Kara Sea with main wind directions from S to SW. In summer, however, an anti-cyclonic vorticity forms winds of N to NE directions in the southern Kara Sea (Harms and Karcher, 1999). This causes a NW off-shore surface flow. Strong off-shore surface flow reveals a significant inverse correlation with the bottom counter current

(Fig. 71). At late summer the circulation regime changes from summer to winter. In the first half of August off-shore transport at the surface and on-shore flow at the bottom prevail. The salt intrusion at the bottom of the Yenisey delta develops. In mid August, the salt intrusion disappears and the vertical stratification is eroded. Practically all expeditions were carried out in time of this dramatic change. Harms et al., (2003) advice to do not only the measurement of classical hydrochemical parameters, but also the observation of meteorological conditions and resulting water circulation. Such type of observations is not available and makes the interpretation of the data difficult.

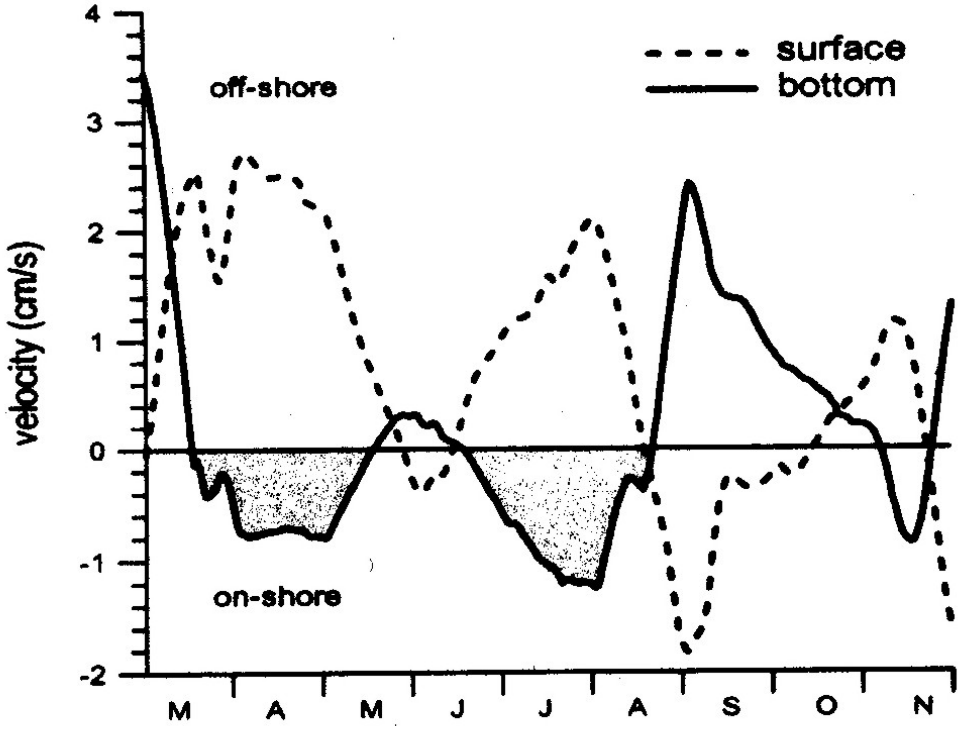


Figure 71 Time series of de-tided bottom and surface flow in the outer Yenisey Estuary, near Dikson from 1-th March to 30-th of November, climatological year (HAMSOM/VOM). Shaded areas denote periods and strength of on-shore bottom flow (Harmes et al., 2003).

In Table 40 the data on the frontal zones in the estuaries in the period from 1993 to 2003 are presented. Practically all expeditions were carried out in September. In 2001 only the second half of August was covered and the October period in 2002.

In September 1993 in the Yenisey Bay there were two frontal zones observed, on 74°N and towards south from 72°30N (Fig.5).The northern front was exceptionally sharp on a distance of 2.5 km and in the upper 10 m surface layer the temperature changed by 2.5°C and the salinity by 8‰. On the second, wider front the temperature varied by about 3°C and the salinity by 9‰. On the way back, few days later (16-20 September from N to S and 21-24 September from S to N) the northern frontal zone was eroded (Burenkov and Vasil'kov, 1994).

In the following four years, during practically at the same time (17-20 September 1997), STD measurements have shown the absence of a frontal zone in the Yenisey Bay. However, it is necessary to note that the hydrological transect was ended at 73°32N (the front of 1993 was at 74°N). In the following years (1999, 2000-2003) the frontal zones were detected in the Yenisey Bay but their location and significance (grad T and S) varied highly (Fig.6).

In the Ob Guba a similar picture was observed. In 1993, at the end of September (24-29.), a wide frontal zone (71-73°30N) with weak gradients of 0.017°C/km and 0.055 ‰/km in the surface layer and 0.042°C/km and 0.16 ‰/km in 10m depth was revealed (Fig.4).In 1997 (13-15 September), the frontal zone was found between 72°30 and 72°50N with gradients of 0.07°C/km and 0.3‰/km. A week later (22-23 September), it had disappeared.

In 1999, 2001 and 2002 the weak frontal zones were found in a range of latitudes of a wide frontal zone of 1993.

So, significant changeability of hydrological structure of water column in both estuaries was observed. The reasons of these variations are quite obvious. These are inter-annual and seasonal variations of river discharges, meteorological conditions, and wind stresses that form the phenomena of surge and outflow and mixing of fresh water plumes, as well as the tidal influence. Related to differences between two estuaries, Harms et al (2003) consider that "although the wind stress may vary slightly between Ob and Yenisey, the overall meteorological situation is very similar for both estuaries and cannot be responsible for large spatial variability. The observed and simulated differences between Ob and Yenisey in terms of vertical stratification and intensity of salt intrusions must be attributed to the different topography and the tidal influence, in particular tidal mixing".

Hydrological structure has an important meaning from geochemical positions because namely in the areas of the frontal zones the most significant changes of concentrations of chemical elements and components takes place. Very fast (few days) changes of hydrological structure of the estuaries strongly complicate the interpretation of geochemical and hydrochemical data because the time frames of the measurements in the expeditions are appeared to be wider than the frames of the variations of hydrological regime.

5.7.2 Biological activity in the estuaries

To understand adequately the geochemical and biogeochemical behaviour of the elements and components in the estuaries it is desirable to have information about the biological activity in the areas studied. It includes data on concentration of Chlorophyll a (Chl a), biomasses of phytoplankton and zooplankton, primary production and biomarkers.

A comparison of the results of three expeditions to the Kara Sea (BP-1997, 1999 and 2000) on phytoplankton biomass, distribution of Chl a and species composition (cell number) was presented in Nothig et al (2003). The data on Chl a concentrations, PP of phytoplankton and biomass of zooplankton in the Ob and Yenisey Estuaries in September 1993 were published in Vedernikov et al., (1994) and Vinogradov et al., (1994).

Preliminary results of phytoplankton species distribution during BP-2001 are given in Larionov (2002), and in Bende and Nothig (2002) the phytoplankton biomass and production in both estuaries is published. Preliminary data on phytoplankton species at 4 stations in the Ob Estuary in September-October 2002 (BP-2002) were shown in Larionov (2003).

Comparative data on Chl a concentrations in the Ob and Yenisey Estuaries between 1993 and 2001 are given in Table 41. It reveals that the most biologically active was 1999 when phytoplankton bloom was detected in the Ob Estuary.

High Chl a concentrations were measured in freshwater in the southern parts of the estuaries. A maximum of 21.7µg/l was detected in the Ob Estuary (station 4418, salinity 0‰). In 2000 the measurements were repeated at these parallels in the Yenisey Estuary. Chl a was in a range 1->3µg/l in 2000 compared to 4.5-5.5 µg/l in 1993. The majority of data were obtained for the middle parts of the estuaries between 72 and 74^0N. In the Ob Estuary, the highest Chl a concentrations were detected in 1999 while in other years (1993, 1997, 2000 and 2001) they were more or less comparable.

In the Yenisey Estuary Chl a concentrations in 1999 were also higher than in other years but not as much as it was in the Ob Estuary. In 1993 and 1997 the concentrations were comparable, and in 2000 and 2001 a little lower than in other years.

In comparison, the Yenisey Estuary is richer by Chl a than the Ob Estuary in 1993, 1997, 2000 and only in 1999 Chl a concentrations were higher in the Ob Estuary. However, the differences are insignificant.

The integral biomass of Chl a from top to bottom for the stations on the Ob transects is highest in 1999 with 95.4 mg/m^3 at 72-74^0N and 135.5 mg/m^3 at 74-76^0N, and on the Yenisey transects is 12.8 and 6.0 mg/m^3 in 1997 and 2000, respectively. In the Yenisey Estuary maximum biomass was measured in 1999 (32.8 at 72-74^0 N and 49 at 74-76^0 N), and only 21.5 and 9.9 (72-74^0 N) were found in 1997 and 2000. High biomass was measured in the freshwater part of the Yenisey Estuary in 2000 with 48.9 mg/m^3(Nothig et al, 2003).

Lebedeva et al., (1994) developed a pelagic ecosystem model of the Kara Sea functioning based on literature data and material from the 49-th cruise of the R/V "Dmitry Mendeleev" (1993). The model allows describing seasonal dynamics of phytoplankton, bacteria, protozoans, small zooplankton, large euryphagous animals and predators, as well as autochthonous detritus and DOM in the north and south-west Kara Sea. It shows the beginning of the productive period in June in the southern and in July in the northern Kara Sea. The main reason for the declining phytoplankton productivity is the decline of nutrients after the water stratification.

Nothig et al., (2003) consider that there are at least two possible explanations for the differences in biomass during the three years. The works in the BP-1999 expedition were carried out somewhat earlier in the year than BP-1997 and BP-2000 expeditions. Higher river discharges with higher nutrient freight were found in 1999. In addition, the main river run-off of Ob and Yenisey Rivers started about one month later in 1999 (Fig.72). So, nutrient-rich freshwater delivered later in the year to the shelf led to the phytoplankton bloom. Different seasonal signals of phytoplankton development during 1999 and 1997/2000 were also found.

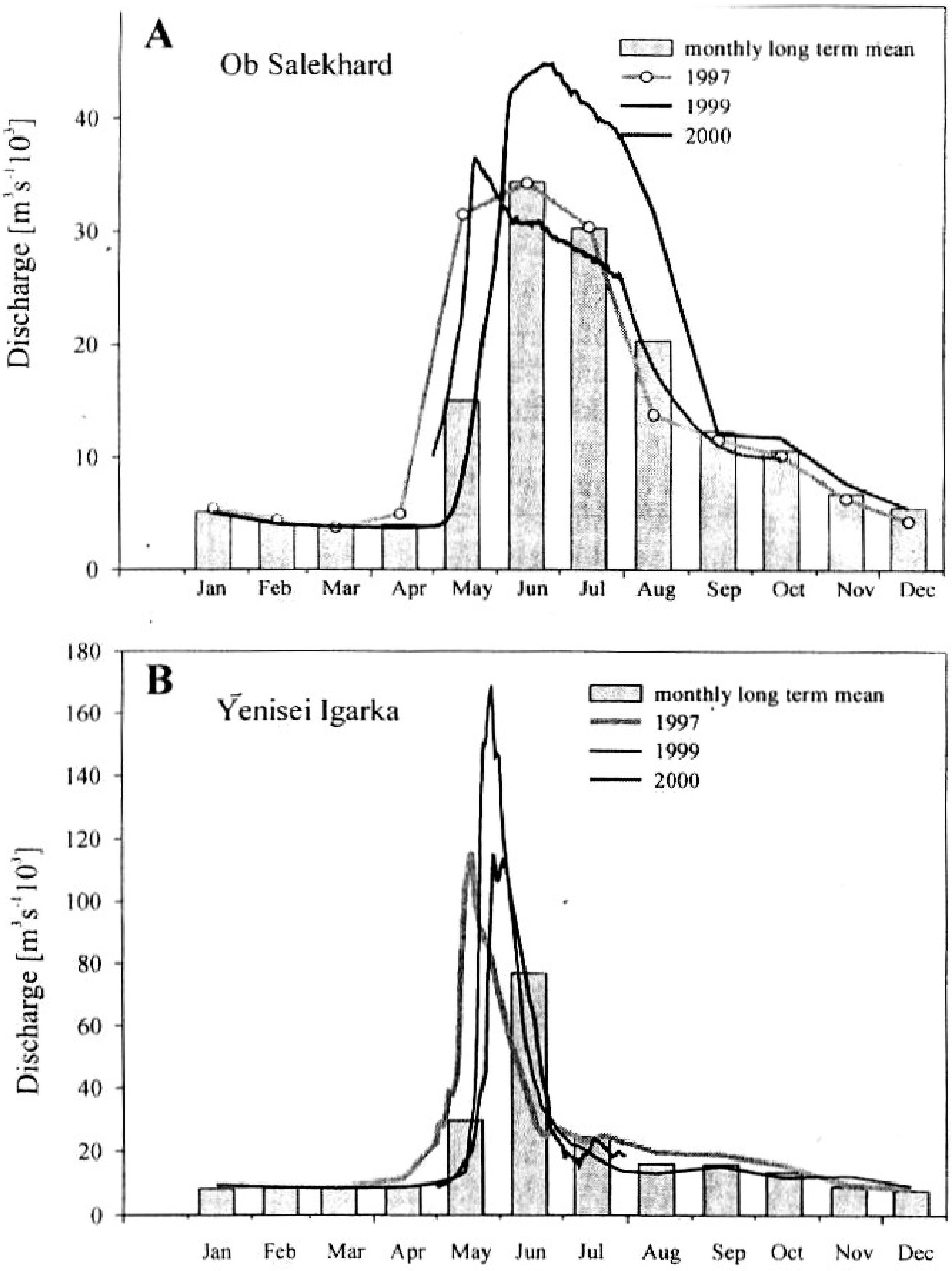


Figure 72 Hydrographs at the downstream gauge stations Salekhard (Ob) and Igarka (Yenisey). Lines represent the discharge of the year during which samples were taken columns represent the long term monthly mean discharge (Kohler et al., 2003).

Species counting reflects the phytoplankton biomass distribution (Nothig et al, 2003). Three to four main populations were distinguished in surface waters. Freshwater diatoms (mainly in the Ob) and diatoms with blue-green algae were found in freshwater parts of the estuaries. Centric and small pinnate diatoms mainly brackish species dominated at 72-74^{0}N. To the north of 74^{0}N brackish/marine species dominated. In the bloom of 1999 in the Ob Thalassiosira cf punctigera and Chaetoceros spp prevailed.

Nothig et al.,(2003) conclude that “the yearly fluctuation of freshwater run-off of both rivers seems to have the strongest influence on the timing and duration of phytoplankton blooms, species composition and biomass standing stocks during summer”.

The primary production of phytoplankton in the Ob and Yenisey Estuaries was measured in the DM-1993 only (Vedernikov et al, 1994), and comparison of PP in different years is not possible. PP in the Ob Estuary in September 1993 was 25-63 mgC/m^2.day while in the Yenisey Bay PP values were significantly higher with 107-312 mgC/m^2.day (see section 4.3.2.4). One of the reasons for low PP in the Ob Guba was unfavourable meteorological conditions (low insolation) for photosynthesis at the time of work. Taking into account the unstable meteorological and hydrological conditions in the estuaries we may assume that in other situation PP in the Ob Estuary would be much closer to PP values in the Yenisey Bay.

In general, PP in these two estuaries as well as in the open Kara Sea is low. The Kara Sea is an oligotrophic water body: in September 1993 PP was lower than in the poorest ocean regions (Sargasso Sea) (Vinogradov et al, 1994).

5.7.3 Behaviour of dissolved elements and components

Major elements

All the available data on the major ions in the estuarine zones of the Ob and Yenisey Rivers testify their conservative behaviour (Section 4.3.2.1). It doesn’t mean that no chemical processes take place here. It was shown (Fig. 51) that the ion exchange between the particle surface and the dissolved load resulted in an increase of Na/Al, K/Al and Mg/Al ratios and a decrease of Ca/Al in SPM of the Yenisey Estuary with growing salinity. Mg, K and Na are adsorbed by the riverborne SPM and Ca is replaced and enters the dissolved fraction (Beeskow and Rachold, 2003). But on the background of high concentrations of the major dissolved cations this process is not practically possible to detect after routine analyses.

DOC

Available information on DOC (Section 4.3.2.2) again shows a linear trend with decrease of the concentration from river water to sea water in both estuaries. As in case with major cations the mixing experiment indicated very small DOC losses at salinity <5%o on about 3% (Kohler et al., 2003). A cross-flow ultrafiltration with separation of colloidal form of DOC has shown that namely this fraction was responsible for redistribution of DOC forms in the estuaries. The colloidal fraction was 30-60% of total DOC in the Ob and 30-45% in the Yenisey (Dai and Martin, 1995).

Nutrients

Significant variations of river discharge, meteorological conditions, snow cover, melting rates, existence and location of frontal zones in the estuaries, concentrations of nutrients and their fluxes result in the important variations of Chl a concentrations, plankton biomass and primary production (PP) in different years. Direct comparison of the data is complicated by different periods of time and by salinity range in transects along the estuaries. Nevertheless, there are some common features in nutrient behaviour in two estuaries.

As a rule, river water is enriched by nutrients and this is an important source of nutrients in estuaries. In the frontal zone areas with sharp gradients of S and T a significant decrease of nutrient concentrations occur due to increase of water transparency and active capture of nutrients by phytoplankton. Sometimes the concentrations decrease to zero, so the nutrients might be the limiting factor for biological activity. A nutrition decrease is also promoted by sedimentation of dead river plankton, co-precipitation with suspended matter of newly formed organic and inorganic colloids. They continue to diminish because of dilution of transformed fresh water with saline waters (Tokarev et al., 2003). An active re-mineralization of OM and dead plankton in the water column results in significant enrichment in bottom water at salinity > 15-30‰.

1993. The data were obtained in period from 15-th to 30-th of September along transects in both estuaries in a salinity range from 0 to 24‰ in the surface layer. In the Ob Guba a wide hydrological front with low T and S gradients was found while in the Yenisey Bay there were two hydrofronts – one South of $72^0$30 N (S~1-10‰) and a very narrow (2.5 km) and sharp front near 74^0N with a strong T and S gradients. From a point of view of biological activity this year was typical one (Table 41).

The NO_3-S dependence in the Ob Guba shows (Fig.47) that the high concentrations (2-4 µM) in fresh water sharply (10-20 times) decrease after passing the hydrographic front (0-0.24 µM) and further remain at this low level. The near bottom samples with S>20-25‰ are enriched in nitrates up to 2µM due to mineralization of OM. A similar picture was observed in the Ob Guba for PO_4 distribution, although the decrease in concentration was not very sharp (5-10 times).

In the Yenisey Estuary nitrate concentrations were low (0-0.4 µM) in freshwaters already and decreased 2-3 times after the first frontal zone and were stable at level 0.00-0.06 µM up to S=24.5‰ in surface waters (the location of the second frontal zone was not fixed here). Low NO_3 and high NH_4 demonstrate an active consumption of phytoplankton by zooplankton. Nitrate is probably the limiting factor in the Yenisey Bay. However, the near bottom water appears to be enriched in nitrates by up to 8-9 µM.

The PO_4 distribution shows a different pattern. Its concentration increases from 0.1-0.3 µM at low salinity up to 0.3-0.5 µM at salinity 20-24 ‰, even in surface waters. Higher PO_4 concentrations were found in deep saline waters (up to 2µM). The probable explanation is the increasing rate of phosphate turnover as a result of higher PP and the intensity of OM degradation in near bottom waters of the Yenisey Bay.

The disappearance of the second frontal zone at 74^0N one week later after the first crossing of the estuary might be connected to the rebuilding of the hydrological structure from summer to autumn regime. This rebuilding might complicate the nutrient distribution.

The silica distribution in both estuaries was of quasi-conservative pattern. The main difference between the two rivers is the lower silica concentration in the Ob (50.5 µM against 83.2 µM).

1997. The works were done in the Ob Estuary in narrow salinity range (3-19‰) in surface waters: 13-15 September and in back way of the ship 22-23 September. At the first period the hydrofront was found at $72^0$30-$72^0$50N, the next week the front disappeared. This may point to the rebuilding of hydrological structure from summer to autumn. In the Yenisey Bay also the works were carried out twice: 17-18 and 19-20 September and in both cases no hydrological fronts were found. This year was similar to 1993 with respect to Chl a concentrations, total phytoplankton biomass was 12 mg/m^2 in the Ob and 22 mg/m^2 in the Yenisey (Nothig and Kattner, 1999). Data on nutrients are scarce and only from the surface layer. The NO_3 concentrations at S=2.4‰ was 1-2 µM and after the passing the frontal zone decreased to 0.3-0.6 µM. The transect along the Yenisey Estuary had four stations only, which is little to construct reliable distribution.

The PO_4 concentration in the Ob Estuary slightly decreased from 0.5-0.7 (S< 10‰) to 0.3-0.5 µM at higher salinity, in the Yenisey Bay four samples gave values between 0.13 and 0.44 µM. Silica in the Ob Guba was quite stable in the whole range of salinity (2.4-20.8 ‰), whereas in the Yenisey a Si decrease with salinity took place (at S=1.2‰ Si=76.5µM).

1999. The BP-1999 expedition was carried out earlier that all previous expeditions- from 24 August to 8 September. As in 1997, the transects were relatively short: in the Ob Estuary 72- $74^0$30N with salinities at surface between 1.8 and10‰ and 2.6-7.4‰ in the eastern and 4.7-12.7‰ in the western Yenisey transect. The frontal zone in the Ob Estuary was detected near 73^0N and near the end of the Yenisey transect at 74^0N. It is possible that the rebuilding of hydrological structure was not started yet (Harms et al., 2003). Moreover, it was possible to observe the period of active phytoplankton bloom with high Chl a (> 5 µgC/l) and biomass production (70-180 mg/m^2). In the Yenisey Estuary the bloom was not so obvious, although Chl.a and biomass (10-60 mg/m^2) was high. It was mentioned above that the earlier stage of pelagic system development and higher river discharge in 1999 were connected with the bloom development

The NO_3 distribution in the Ob Estuary shows extremely low concentrations in the full range of salinity, probably related to nitrate consumption by phytoplankton. Only in bottom water nitrate increased to 0.3-0.4 µM due to OM mineralization. The PO_4 concentration in surface water of the southern part of the transect was high (0.5-1.5 µM, one sample 4.5 µM). After crossing of the frontal zone its concentrations were increased, although the phytoplankton bloom took place here. It is possible to admit that for domination of diatom bloom (>90%) nitrogen was more important than phosphate, while in the Yenisey Bay the bluegreen algae and chlorophyte (>50% of the population) dominated. Similar situation was in the Yenisey Bay: NO_3 concentrations were decreased (<0.02-0.08 µM) while phosphate concentrations slightly decreased from 0.5 to 2.5 µM. It is probably phosphate was more important for bluegreen algae and chlorophites than it was for diatoms.

An unusual distribution of dissolved silica in both estuaries was observed in 1999. The river water samples were unfortunately absent in this case. Si concentrations in surface waters at S=2-15‰ in both estuaries reveal an increase from 5-10µM to 20-23 µM (in one sample 40 µM). Deep and near bottom samples show significant scattering, especially in the Ob. It is impossible to explain this Si behaviour because a Si decreasing due to diatom consumption would be expected.

2000. The expedition BP-2000 focused mainly on the Yenisey Estuary (5-19 September) covering the wide region from 70 to 77^0N in a salinity range from 0 to 27‰ in surface waters. A clearly defined hydrofront was detected at $72^0$40-$73^0$30N with T gradient ~0.5^0C/km and S gradient of 0.2‰/km. Chl.a and integral biomass concentration was a little lower than in 1997 and 1999. NO_3 in river water varied in a range from 0.06 to 3.1 µM, although up to the hydrofrontal zone at S=7-8‰ its concentrations were near 1µM. After its crossing NO_3 diminished slightly to 0.5-0.8 µM. In near bottom waters at S>25-30‰ OM degradation resulted in nitrates increase to 4-6 µM.

The PO_4 concentration before the hydrofront was 0.5-0.8 µM and decreased behind it to 0.1-0.3 µM (near bottom 1-3.5 µM). The weaker phytoplankton development compared to 1997 and 1999 did not result in significant drop of nitrate and phosphate concentrations, as it has happened in previous years.

The Si concentrations decreased with salinity although the scatter was still large. Its concentrations were in a range from 60 to 140 µM and in average 107 µM.

2001. The extensive works were carried out in the Yenisey Estuary in period 18-23 August and in the Ob Estuary 7-11 September. S Sampling was performed in a salinity range in surface waters from 1 to 10‰ in the Ob, and 0-27‰ in the Yenisey Estuary. The frontal zone in the Yenisey was clearly defined at 72-$72^0$30 N with moderate T and S gradients. In the Ob Estuary the hydrofront was located between $72^0$40 and $73^0$10 N and was a little weaker. Chl a varied around 1 µg/l between 73 and 75^0N (data on integral biomass are absent). This is lower than in the previous years.

The NO_3 concentration in Ob fresh water varied in a range 0.15-0.40µM. After crossing the frontal zone (S=1-10‰) the concentrations decreased to 0.05-0.15 µM. NO_3 increase in near bottom waters was low with up to 0.4µM.

The PO_4 concentration was 0.6-2.0 µM at S = 0 and decreases to zero after the frontal zone. Regeneration of OM near bottom resulted in small phosphates increase (up to 1µM).

The Yenisey water contained 0.12-0.30 µM of NO_3. The samples with S>5‰ were not collected in this cruise. PO_4 concentration in river water was 0.6-1.6 µM. Near bottom saline water showed similar PO_4 concentrations and higher than at S=0 NO_3 concentrations – 0.6-1.1 µM.

The Si concentrations in the Yenisey River water were 68-124µM and average 101 µM. They decreased quasi-linearly with salinity. In the Ob Guba very few samples analysed showed significant scattering, although in general Si decreased with salinity.

The main conclusions regarding nutrient distribution in the two Siberian estuaries are:

- ☐ There are more similarities than differences between the estuaries. Seasonal river discharge variations and meteorological conditions influence the nutrient behaviour. The nutrient distribution determines an activity of phytoplankton, and, in its turn, it is determined by an activity of phytoplankton. In this relation 1999 is clearly distinguished from other years. In the Ob Estuary, and to a smaller extent in the Yenisey Estuary a powerful phytoplankton bloom was detected, which resulted in the almost full utilization of nitrates. The bloom influence is much weaker on the PO_4 distribution in both estuaries.

- ☐ The degree of bioactivity can be brought in the following order: **1999>1993=1997=2000>2001**. This order is valid for both estuaries. The bioactivity was somewhat higher in the Yenisey in 1993, 1997 and 2000, and only in 1999 the bloom was higher in the Ob Estuary. In agreement with that, the nutrient concentrations in the Ob was higher in 1993, 1997 and 2001, however, in 1999 NO_3 was near zero in both estuaries. That suggests that nitrate is more important for phytoplankton than phosphate. Dissolved silicates, excluding the anomalous in 1999, were always higher in the Yenisey.

The PP measurements, which were carried out in 1993 only, demonstrated higher productivity in the Yenisey Estuary. However, it is not clear that the same situation would occur in other years.

Dissolved trace elements

The behaviour of dissolved Fe, Cu, Cd, Ni and Pb in the Ob and Yenisey Estuaries was studied by Dai and Martin (1995), Sr, F and B by Savenko et al (2001), Fe, Mn and Sr by Beeskow and Rachold (2003), Hg by Cossa et al (1993) and Couquery et al (1995), and Ba by Guay and Folkner (1998).

In the following the behaviour of the elements in the estuaries is compared and the level of their involvement into the biological processes qualitatively estimated. No difference was found in the behaviour of Sr, F, B, Fe, Cu, Pb, Hg and Ba. Only Ni and Cd have demonstrated difference in their behaviour.

Ni behaves conservative in the Ob Estuary and non-conservative in the Yenisey Bay (September 1993). Some excess at S<10‰ in the Yenisey Bay (Fig.48 C) is a result of biological regeneration process (Dai and Martin, 1995). This hypothesis is supported by the close relationship between nitrates and truly dissolved nickel (R^2=0.84). The correlation is absent between NO_3 and colloidal Ni, which suggests that additional Ni has the same origin (generated from OM) as nitrate whereas colloidal Ni is primarily associated with OM (for $Ni_{coll.}$- $C_{org.coll.}$ R^2=0.84 in the Ob and 0.81 in the Yenisey).

Cd has complex distribution in both estuaries (Fig.48 B). Coefficient of correlation between dissolved Cd and nutrients is 0.78 for Cd-NO_3 and 0.54 for Cd-PO_4 in the Yenisey. In the Ob, the Cd-NO_3 correlation is 0.49 whereas no correlation exists between Cd-PO_4 (Dai and Martin, 1995). This suggests that the Cd behaviour is a result of the biological processes (nutrient regeneration).

So, the data on dissolved trace elements show that Ni and Cd among other metals have been evolved in the association with nutrients more active in the Yenisey than in the Ob Estuary. The biological activity was more extensive in the Yenisey Estuary in September 1993 (higher Chl a concentrations and higher PP). It would be interesting to compare this result with that of 1999, when the phytoplankton bloom was found in the Ob Guba, but data on dissolved trace elements are absent.

5.7.4 The behaviour of SPM and particulate elements and components

SPM concentrations

The SPM concentrations in the Yenisey River were always lower than in the Ob River, and after the constructions of great hydrological stations (dams) at mid of 50-th of the last century in both rivers a sharp drop of annual SPM concentrations was observed in the Yenisey River.

The Ob Estuary differs from the Yenisey one by longer length and width, shallower depths and smaller water currents (Table 39). This results in faster and fuller sedimentation of river SPM. The works in the Ob Guba were carried out in September 1993, September 1997, August 1999 and September 2001. However, only in 1993 the full salinity range in surface waters (0-24‰) was covered. In 2001 investigations were started in fresh waters but continued only to a salinity of 9.8‰. In 1997 and 1999 the transects were started from 2-3‰ and finished at 15-20‰. Only for 2001 a reliable transect of SPM distribution can be drawn.

1993. The SPM concentrations in the Ob River was in a range 7-115 mg/l, in average 35.5 mg/l (n=11). However, station 4418 has abnormally high SPM concentrations (73-115 mg/l) which is probably caused by the lateral input from shoreline and due to bad weather conditions during sampling. Excluding this station from calculations, the average SPM is only 13.8 mg/l. The SPM concentration decreased gradually to 2-4 mg/l after 20‰ in surface water but increased up to 15 mg/l near bottom at high salinity (>30‰) due to resuspension of bottom sediments. A similar distribution was found in the Ob Estuary in 1997 (4-8 mg/l at S=3-5‰ and 0.5-0.8 mg/l at S=18-21‰). In 1999, at time of phytoplankton bloom, the SPM concentration was 6-18 mg/l at S=1.8-3.3‰ and decreased further to 1-5 mg/l in the area of the hydrological front (one sample was 29.5 mg/l). Samples with salinity higher than 10‰ were absent in surface waters. Near bottom a scattering from 0.4 to 33.7 mg/l (even up to 94.8 mg/l at S=25-34‰) was observed. Few samples on the Ob-2001 transect showed 12-19 mg/l at S=0. There were 3 samples only with salinity more than 2‰.

A generally similar situation was observed in the Yenisey Estuary in. In fresh water, the SPM was always lower than in the Ob River: 1993- 2.6-14.0 mg/l, av. 4.8 mg/l, 1997-1.0-4.5 mg/l at S=1.2-4.2‰, 1999- 2.0-15.0 mg/l at lowest salinity 4.5-5.0‰, 2000- 3.0-9.5 mg/l, av.4.5 mg/l, and in 2001 2-5 mg/l, av.3.4 mg/l at S=0. During all expeditions, except BP-2001, SPM decreased with salinity to low concentrations (0.5-1.5 mg/l) and increased near bottom due to resuspension. In 2001, the SPM concentration was surprisingly constant at a level 3-4 mg/l in the full salinity range (0-26‰). Gebhardt et al., (2004) chose this expedition to assess the annual flux of SPM and POC by the Yenisey River into the sea. The authors conclude that gradient of SPM was absent in the Yenisey Estuary in September 2001 although the samples with S>26‰ were absent. At the same time, in Fig. 2 of their paper SPM concentrations in surface waters at salinity >25-30‰ were decreased to 1.5 mg/l and lower. It is, in fact, difficult to explain the anomalous SPM distribution in 2001 in comparison to other years because of typical river discharge, meteorological conditions and other environmental parameters in this year. The anomaly of this year is in agreement with data on the Holocene sediment thickness in the Yenisey Estuary (Dittmers et al., 2005). Beginning from 72^0N the thickness reaches 10 m and the full area of the sediment accumulation occupies 72-74^{0}N that is namely the working area during BP-2001 expedition. The suggestion by Gebhardt et al.(2004) that "though the Yenisey River was accumulating sediment before dam construction, the Yenisey River changed into a bypass system after the construction of the dam" is not with agreement with SPM distribution pattern in other years (1993, 1997, 1999 and 2000). Much more probable "another possible explanation that the 2001 August sampling period was not representative of the discharge system of the entire summer: i.e. only during times of high water discharge does the Yenisey River act as a bypass system" (Gebhardt et al., 2004).

Above we have presented the assessments of gross and net river fluxes of SPM (Sections 4.2.3 and 4.3.5). It was shown, based of the 1993 expedition, that in the Ob and Yenisey Estuaries about 89-95% and 80-93% of total SPM fluxes have been lost respectively. The new assessments of SPM delivery by two rivers into the Kara sea by Gebhardt et al. (2004) present by essence the assessments of the net SPM fluxes. However, their salinity ranges is not full (up to 10‰ in the Ob and 26‰ in the Yenisey Estuaries instead of 34‰ at the marine end member). The anomalous SPM distribution in 2001 cannot serve as a representative pattern. The authors of this book evaluated the SPM flux in the river mouth, which is the place of estuarine entrance into the sea, as 3.76x10^6 t/y for the Ob River and 5.07x 10^{6}t/y for the Yenisey River. Our assessment of the net SPM flux of the Ob River is somewhat lower (0.8-1.9) x 10^{6}t/y as it takes into account the full salinity range. However, our assessment of the net SPM flux of the Yenisey River – (0.3-0.94) x10^{6}t/y is much lower and not comparable, because Gebhardt et al., (2004) assessed the untypical data of anomalous 2001 .

The main differences between the Ob and Yenisey are consisted in:

1) lower and less variable SPM concentrations in the Yenisey;

2) sharp peaks of SPM discharge in period of spring flood;

3) more extensive process of sedimentation in the Ob Estuary.

Particulate organic carbon, nitrogen and phosphorus

Absolute POC concentrations (in mg/l) correlate positively with SPM (Fig.52 A) while its relative content (in %) demonstrates another pattern.

1993. In the Ob Estuary the POC was 7-10% in the river end member, 5-10% in the frontal zone (1-16‰), and after crossing this zone POC concentration dropped down to 5-7% at S=17-22‰. A low POC content was found in near bottom SPM (3-5%).

The typical content in fresh water of the Yenisey Estuary was 8-15%. In the first frontal zone (1-10‰) a high scatter of POC was observed (from 4 to 15-27%). After the second very narrow and sharp hydrological front POC increased to 15-40% (S=13-21‰) and remained at a high level (10-25%) in the intermediate waters with salinity>25‰. The POC content was low in near bottom SPM (2-7%).

1997. The POC content was near 8-10% at salinity 3-4‰, increased up to 20-30% after the frontal zone and was low again in near bottom SPM (3-7%) on the Ob transect. No frontal zone was found in the Yenisey Estuary in this year. At S<5‰ POC was 5-7.5%

and increased up to 20-26% at S=6-15‰ in surface water. At higher salinity there were near bottom samples only (POC=1.5-4.0%, one sample-9%).

1999. A high POC content would be expected because of the phytoplankton bloom in the Ob Estuary. In reality POC increased from 2-7% before the frontal zone up to 12-24% in the area of the frontal zone (8-10‰). Samples from surface waters with higher salinity were absent. The POC content was 2-3% only in near bottom waters due to resuspension of bottom sediments. In the Yenisey Estuary significant increase of POC was detected from 3-5% up to 23-30% in salinity range 3-8‰. Surface samples with higher salinity were absent. Typical for resuspended SPM, a low POC content (4-5%) was measured in near bottom layer.

2000. In the Yenisey River water the POC content was 5-8% and remained more or less stable in the frontal zone (5-17%). It increased up to 19% at salinity= 20-28‰. Only 3-7% of POC was found in near bottom samples.

2001. There were only few samples on the Ob transect. The POC content was 5-6.5% in fresh water and 0.7-1.7% in near bottom SPM with S=31‰.

This year showed a stable SPM concentrations along the Yenisey transect. Absolute POC concentrations decreased slowly from 0.3-0.5 mg C /l at S=0 down to 0.2-0.25 mg C/l at S=10-27‰. In near bottom layer POC increased up to 0.6-1.3 mg C/l as a result of higher SPM concentrations. The POC content was high (8-15%) in river waters and decreased slowly down to 6-8% at higher salinity. Again, POC was low in near bottom samples (2-4%).

The analyses reveal that:

- ☐ The highest POC content in the Ob River was found in 1999 (12-24%), the lowest in 2001 (5-7%) while in the Yenisey the opposite picture was observed. Here, maximum POC content was measured in 2001 (8-22%) and minimum content in 1999 (3-5%):
- ☐ The highest POC in surface water of the Ob Estuary was found in 1999 at S=15-20‰, and the lowest content in 2001 (7-8% at S=10‰). It is interesting to note that in 1999, the year of an intensive phytoplankton bloom, POC did not exceed 24% in salinity range 5-10‰. In the Yenisey Bay the highest POC content was observed at the same salinity range (5-15‰) in three years- 1993 (15-27%), 1997 (20-26%) and 1999 (20-30%). In 2001, maximum POC content was observed in the river end member (8-22% POC) and the POC content was low (6-8%) at higher salinity (10-26‰).
- ☐ Near bottom SPM samples with high salinity contained low POC (2-4%, sometimes up to 6-9%) as a result of resuspension of bottom sediments with low POC content. This was confirmed by the analyses of biogeochemical indicators (amino acids, amino sugars, AA-derived reactivity index (RI)) which show the intense degradation of near bottom SPM (Unger et al., 2005);
- ☐ The ratios of maximum POC in the Ob and Yenisey Estuaries were close to 1 in 1993, 1997 and 2001 when bioactivity was comparable (Table 41). However, in 1999 with highest bioactivity in the Ob Estuary this ratio was less that 1 (~0.8).

In general, taking the seasonal and inter-annual variations into account, no significant differences in the concentration and behaviour of POC between two Siberian estuaries were observed.

Nutrients

Data on particulate nitrogen (PN) in the Ob (1999 and 2001) and Yenisey (1999, 2000 and 2001) and particulate phosphorus (PPh) in the Ob (1997 and 2001) and in Yenisey (1997, 2000 and 2001) (Beeskow and Rachold, 2003; Gebhardt et al., 2004; Rachold, unpublished data) are available. The distributions of PN and PPh along transects is very similar to POC distribution. There is a positive correlation between POC and PN as well as between POC and PPh. A dependence POC-PN combined two estuaries and two expeditions (2000 and 2001) may serve as an example (Fig. 73). The coefficient of correlation is high with 0.94. The correlation between POC and PPh is also positive but with somewhat lower coefficient. Our calculations show that R^2=+0.547 (n=27) between POC and PPh in the Ob Estuary in 1997 and +0.855 (n=12) in 2001, in the Yenisey Estuary R^2=+0.711 (n=19) in 1997, +0.892 (n=19) in 2000 and +0.874 (n=7) in 2001.

Higher coefficient of correlation between POC and PN is in agreement with the assumption that nitrogen is more important for phytoplankton development than phosphorus.

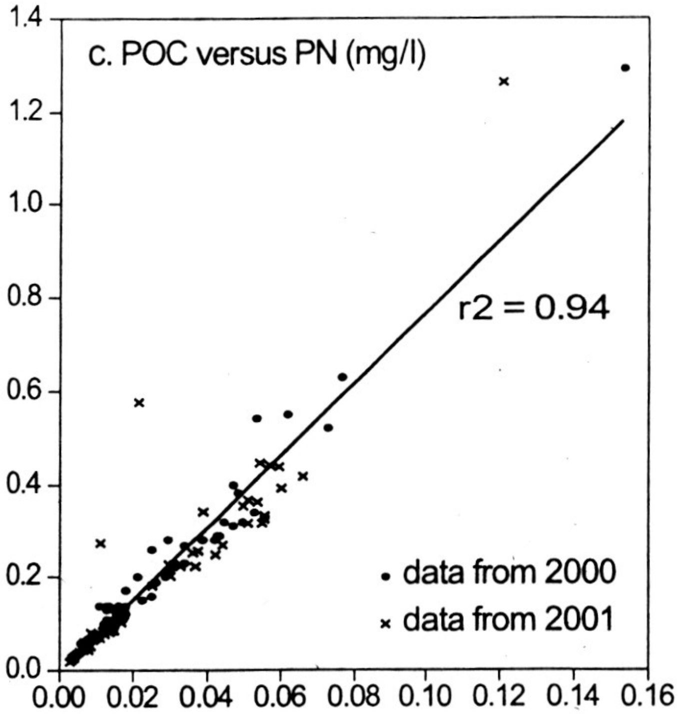


Figure 73 Direct correlation between POC and PN in the Ob and Yenisey Estuaries in 2000 and 2001 (Gebhardt et al., 2004).

C/N ratio

This ratio is generally high in terrigenous OM and low in marine OM and therefore is a useful tracer to distinguish between two main sources of material. The ratio of C/N=18.3 in soils and 25.0 in roots (the samples were taken not far away from the Ob River approximately 5 km north of Salekhard) (Unger et al., 2005). Typical C/N ratios in surface SPM in the estuaries are about 7-9 and in offshore SPM about 7. The distribution of C/N ratios in the Yenisey SPM in 2000 (Fig.54) demonstrates a quite stable behaviour at low salinity 0-5-7‰ and a small decrease after crossing of the frontal zone (5-20‰) to 6-7 (typical for marine plankton). At higher salinity, in near bottom water, C/N ratios were higher with 11-12 and even 16 in one sample. This means that the degradation of labile organics takes place in deep water and its C/N ratio is close to those in bottom sediments (Unger et al., 2005). The authors calculated C/N ratios in surface SPM to be 7.1- 10.8, av. 8.5(n=37), in halocline 5.9-16.7, av. 9.7 (n=25), and in deep water 7.5-14.7, av. 10.3 (n=29). They conclude on a base of their C/N data and biomarkers (Fahl et al., 2003) that the difference between the two rivers are the higher portion of terrestrial OM in the Yenisey region and the higher sediment load in the Ob River.

Major and trace elements in SPM

All available information on the results of expeditions 1993, 1997, 2000 and 2001 reveals that the ratios of major elements Si, Fe, Mg, K, Ca, Ti to Al are very stable (<2) in the full range of salinity. That may due to the relatively low bioactivity in the estuaries. Noticeable differences between the two estuaries were not observed. A decrease of the Ca/Al ratio (1.5-3 times), a slight increase of Mg/Al and K/Al ratios and a significant increase of the Na/Al ratio (up to 5-10 times) with salinity are observed. This is probably due to ion exchange between particle surfaces and the dissolved load.

The data of 1993 for particulate trace elements show similar behaviour of the majority of them in both estuaries although Chl a concentrations and PP were higher in the Yenisey Estuary in this year. In 1997, when bioactivity was a little higher in the Yenisey Bay, the majority of trace elements showed similar behaviour. Only Cr enriched the Ob SPM at salinity 15-25‰ and Mn enriched the Yenisey SPM at S=15‰.

The results of the expedition BP-2000 show (Table 29) a noticeable enrichment of SPM by trace elements. The highest enrichment factor (EF~3) was found for Mn and Cd in the Yenisey Bay at S=20-30‰. The elements of Groups 2 and 3 followed the behaviour of Mn along the transect. The ratio below 1 for Ni, Cu, Zn (Fig. 55) at mid salinity coincides with high dissolved Mn concentrations and its redox sensitive behaviour (Beeskow and Rachold, 2003). Desorption caused by inorganic complexation with the major anions in seawater may explain this element behaviour in the estuary (higher EF at higher salinity).

Unexpectedly stable were the concentrations of all trace elements in SPM of the Ob Estuary in 2001 (Table 30). The opposite situation was observed in the Yenisey Bay. Many elements demonstrated high EF- up to 15 and higher for Cu, Pb, Cr and 6-13 for As, Sr, Ni, Cd, Zn. High EF for the samples with high salinity (26-30‰-near bottom layer) may be partly explained, in analogy with the previous year, by the association of the metals with Mn (its maximum EF was about 6).

So, the data on chemical composition of the Ob and Yenisey SPM in their estuaries show that:

- ☐ As a rule, the enrichment factor (EF) for major and trace elements in SPM was either higher in the Yenisey Bay or was comparable in both estuaries. This conclusion coincides with higher bioactivity in this estuary. However, a positive correlation of the trace metal involvement into the biological cycles with the level of phytoplankton bioactivity is not observed.

- ☐ The physico-chemical processes such as cation exchange, adsorption-desorption and other play probably a significant role in major cations and trace metals behaviour in the mixing zone.

Summary of Section 5.7

A summary is given in the integral form in Table 42.

- ☐ The comparison of biogeochemical processes in the Ob and Yenisey Estuaries in five different years, from 1993 to 2001 (regime of river discharge, hydrological regime, SPM distribution, concentrations and behaviour of DOC, POC, N-NO_3, P-PO_4, SiO_2, PN, PPh, level of bioactivity-Chl a concentrations, phytoplankton biomass, PP, intensity of trace metal involvement into the biological cycles (based on EF)) shows that in majority of the expeditions (1993, 1999, 2001) the integral intensity of biogeochemical processes was higher in the Yenisey Estuary. In 1999 only the situation was the opposite, but it is necessary to note that the available results for this year are incomplete. So, this conclusion needs in more confirmations.
- ☐ The differences presented in 1) are not very significant. The general conclusion is that there are more similarities between the two Siberian estuaries than differences between them.

5.8 Comparable geochemistry of bottom sediments

The main geochemical characteristics of bottom sediments in the Ob and Yenisey Estuaries (facial environments, grain-size, mineralogical and chemical composition including organic and inorganic elements and components) were presented in details and with short comments in Section 4. Now the most important differences in these characteristics between the two Siberian estuaries will be emphasized.

Facial environments

Four facial environments were defined in succession from the South to the North in the Kara Sea (Levitan et al., 1996, 2005):

1) the proper river deposits environment;

2) the facial environments of the Ob and Yenisey Estuaries;

3) the facial environment of inner shelf- the Ob-Yenisey shoals;

4) the facial environment of the external shelf.

The grain-size composition varies from gravel-sandy to silty-pelitic muds in the sediments of the river facie that are characterized by immaturity of material up to very fine pelitic clays. For river and estuarine sediments of both estuaries the bimodal structure of their grain-size distribution are typical. Northward it shows a more uniform pattern with a shift of the two maxima from 20 and 400µm at South to 10 and 100 µm to

North and transforms into mono-modal structure in the northern most area (near 76^0N and northern) (Beeskow and Rachold, 2003).

The most important differences in mineralogical composition between the bottom sediments of both rivers and estuaries are the following. The Yenisey contains a high content of black ore minerals and SKI>2.5 (predominance of smectite over illite among clay minerals), a high ratio of clinopyroxene to epidote, the remains of wood in sandy fraction and very high MS (3000-4000x 10^{-6}SI). The Ob is characterized by low or almost absence of black ore minerals, SKI<2.5, a high content of wood remaining in the sandy fraction and low MS (< 1000x10^{-6} SI).

Paleo-weathering of the Triassic flood basalts of the Putorana Plateau produces smectite-rich soils which are eroded and transported by the Yenisey SPM into the Kara Sea (Schoster et al., 2004). The sediments as well as the SPM of the Ob show lower smectite content than in the Yenisey but higher values compared to the upper continental crust. The source of this material in the Ob drainage basin is not identified yet.

Distribution of TOC in bottom sediments in the estuaries, high C/N ratio (9-14), $\delta^{13}C_{org}$ values and biomarkers demonstrate the predominantly terrigenous origin of organic carbon in both estuaries and its decrease to the North (Stein and Fahl, 2003).

Chemical composition

The ratios of elements to Al for the surface bottom sediments are given in Table 43. The data by Gordeev et al (1995) and Schoster and Stein (1999) in this table are in agreement. The Mg/K ratios in bottom sediments are very similar to those in SPM of the estuaries. In the Yenisey sediments it is two times of the Ob sediments. The Mg/Al and Ca/Al ratios are higher and K/Al ratio is lower in the Yenisey sediments while the Fe/Al and Ti/Al ratios are comparable in both estuaries. Among the trace elements the ratios Ni/Al, Cr/Al and V/Al are higher and Zr/Al, Sr/Al and Rb/Al are lower in the Yenisey bottom sediments. The differences between the ratios of trace metals to Al content in bottom sediments are not as significant as in SPM.

The data by Miroshnikov and Asadulin (1999) show that the Ce and Rb content in Ob sediments is higher than in the Yenisey sediments (64 µg/g versus 48µg/g and 96 µg/g against 69 µg/g respectively). The data by Krasnyuk and Vanshtein (1999) and Levitan et al., (2002) confirm these results.

All available data on bottom sediments and SPM reveal that their compositions reflect the input of sedimentary material from the large trap basalts of the Putorana Mountains and the deposits of the West Siberian Lowland to the Yenisey Estuary, and metamorphic Quaternary deposits of the West Siberian Lowland are the main source of material to the Ob Estuary. This conclusion was drawn also in previous publications (Duzhikov and Strunin, 1992; Schoster and Stein, 1999; Schoster et al., 2000 and other)

Viccosy-Shirley et al.(2003) show that the Siberian shelf surface sediments are the mixture of four end member compositions that can adequately describe the variable chemistry of sediments. These are:

1) shales;

2) basalts;

3) mature sandstones;

4) immature sandstones.

To indicate this, the authors have used the scatter plots of single and multiple element ratios. We use this approach also to the Ob and Yenisey sediments (Fig.74). Basalts have the highest Mg/K ratio; sandstones, the coarse-grained sedimentary rocks, have the highest Si/Al ratio; shales have both, low Si/Al and Mg/K ratios. Strong differences of the sediments of two estuaries are revealed. The Yenisey sediments are the mixture of the basalt and the shale end member with minor input from the sandstone end member while the Ob sediments are the mixture of the shale and sandstone end members with minor input of the basalt end member. These results are in agreement with the chemistry and mineralogy of the estuarine SPM and coincides practically with the conclusion made by Schoster and Stein (1999).

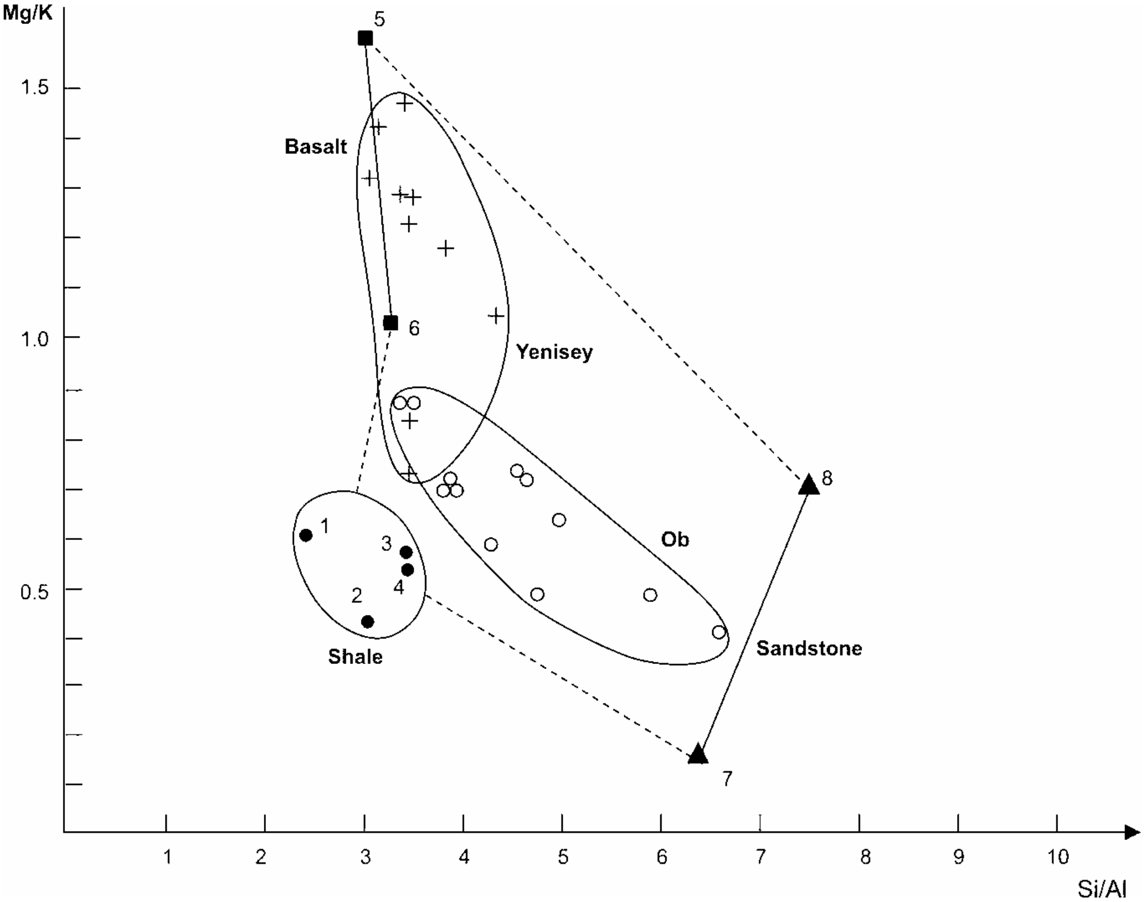


Figure 74 Mg/K against Si/Al in the surface bottom sediments of the Ob and Yenisey Estuaries. 1-8 – references.

A direct comparison of Ob (70-73^{0}N) and Yenisey (71-73^{0}30N) estuarine sediments reveals (Fig. 75) that the Yenisey sediments are enriched by Ca, Mg, Sr and Ni due to sediment supply from the trapp basalts from the Putorana mountains. The Ob Estuarine sediments contain more K, Rb, Ba, Pb, Si and Zr. Schoster and Stein (1999) consider that as a result of depletion in the Yenisey Estuary's sediments because of dilution of its SPM supplied from the Western Siberian Lowland with material from the Putorana Mountains. Although the Ob sediments are mainly a mixture of shales and sandstones, the content of the whole group of the elements (P, Mn, Ca, Na, Fe, Cr, V, Zr, Zn, Si, Ti) appeared to be higher than in an average shales. A possible explanation could be a fractionation due to water currents when the material with heavier and larger minerals accumulated mainly in the estuaries (Si, Zr, Ti, Cr). The capture of some elements (Co, Zn, Pb) by Fe- and Mn- hydroxides could result in the enrichment of these elements in sediments. The depletion of the Ob SPM in orthoclase and enrichment in plagioclase may explain the higher Ca, Sr and Na in sediments (Schoster and Stein, 1999).

So, the differences in mineralogical and chemical composition of the Ob and Yenisey Estuaries and the reasons of it are quite evident.

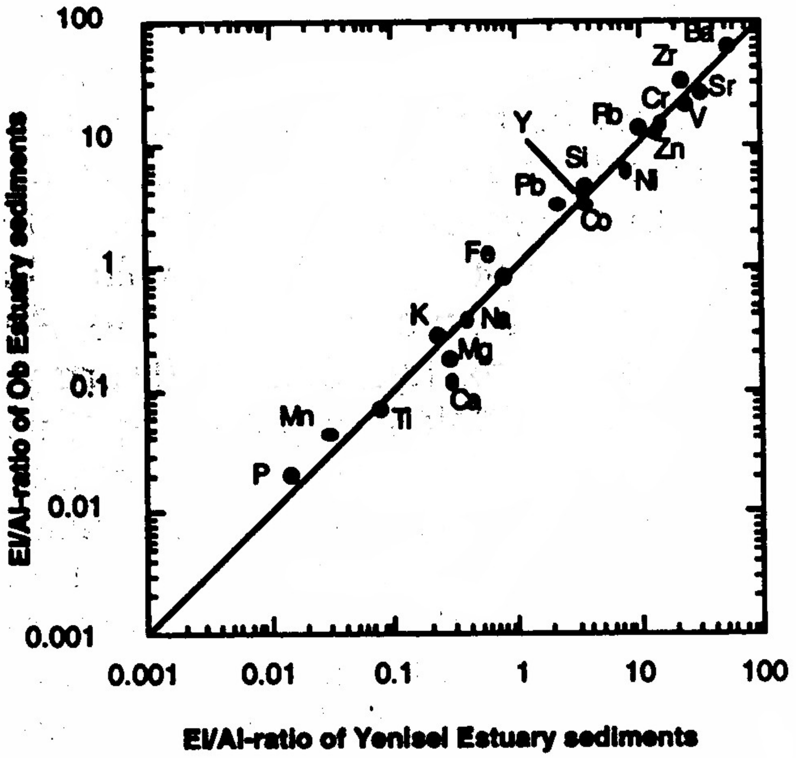


Figure 75 Comparison of the Ob and Yenisey surface sediments (Schoster and Stein, 1999).

6 Conclusion

The results of the comparable study of geochemical features of the Ob and Yenisey Estuaries based on the data of seven big expeditions and several small expeditions for the period between 1993 and 2003 and all available published materials may be shortly formulated as the following.

River discharge

The two biggest Arctic rivers- Ob and Yenisey- have practically equal areas of the watersheds and differ slightly in water discharge (The Yenisey is 1.5 times more abounding in water) and SPM discharge (SPM flux of the Ob River in 3.4 times higher). The review of the data on river and SPM discharges for the last 60-70 years reveal that maximum changes of the Ob water discharge reached 20% of its multi-annual average value. Small positive trend takes place for this period (+5%), while the SPM discharge near Salekhard remains quite stable. The Yenisey water discharge slightly increased (+6%) also, however the SPM flux of the Yenisey decreased significantly (in 2.8 times) due to the constructions of big dams in its upper and middle reaches in mid of 60-th of the last century.

Basin's characteristics

Both rivers (length of the Ob- 3650 km, of the Yenisey- 3490 km) cross different climatic zones from South to North. Significant parts of their watersheds and estuaries are located in the Arctic with very cold continental climate with winter's temperatures -40-50^{0}C. The multi-annual permafrost-permeated rocks are widespread over the two basins and have substantial impact on water balance. They play the role of a water-resistant layer which increases the specific water balance.

The differences in geological characteristics of the two watersheds, presence of the basalts of the Putorana Plateau in the NE part of the Yenisey watershed first of all, result in significant distinctions in chemical and mineralogical composition of SPM and bottom sediments of both rivers and their estuaries.

River water chemistry

No significant distinctions in composition of dissolved major and trace elements and organic carbon exist between the rivers (they are close to the global concentrations). The carbonate weathering is dominated in the watersheds of both rivers. The Ob River waters are enriched in nutrients (nitrates and phosphates), while the silica concentration is higher in the Yenisey River waters.

Estuarine-deltaic areas

The estuarine-deltaic areas of the Ob and Yenisey have similar origin. Postglacial transgression of the World Ocean resulted in the flooding of the erosional river valleys that were formed in the conditions of the sea regression. As a result the ingression bays were formed (Obskaya Guba and Yeniseyskiy Zaliv (Bay)). Relatively small deltas are forming at the tops of the bays. Both estuarine-deltaic areas are stretching South to North. The Ob Guba is twice longer and 2-3 times wider and shallower than the Yenisey

Bay. It means that in the Ob Bay the conditions for sedimentation processes are more favourable.

Hydrology

The historical data show a permanently existing pycnocline in the estuaries of both rivers. The differences of hydrological regimes in the two estuaries are quite evident. The frontal zones in the Ob Estuary are not such sharp as in the Yenisey Bay. More pronounced intrusion of saline waters near bottom in the Yenisey Estuary than in the Ob Estuary is a result of several reasons. Firstly, it is a result of the tidal mixing which is weaker in the Yenisey Estuary. Secondly, different shape of the sea bed: deeper and narrower in the Yenisey and broader and shallower in the Ob. The third point is the geographical orientation of the estuaries: the prevailing NW winds in summer coincide with the Yenisey Estuary orientation that results in a maximum off-shore fresh water transport in surface layer which creates the near-bottom intrusion of saline waters.

There are the significant variations of the hydrological structure of water columns in the estuaries. The inter-annual and seasonal variations of river discharge, meteorological conditions, wind stress, the tidal influence are the main reasons of these variations. The interpretation of hydrochemical and geochemical data is very complicated because the time frames of the measurements in the field works are wider that the time scale of the hydrological variations.

Biological activity in the estuaries

The biological characteristics (Chlorophyll a concentration, biomass of phyto- and zooplankton, primary production (PP), biomarkers) have been measured in the expeditions to the Ob and Yenisey Estuaries and the adjacent Kara Sea (PP was measured in DM-93 expedition only).

The highest Chl a concentrations as well as the integral biomass from top to bottom were detected in the Ob Estuary in August 1999 when phytoplankton bloom took place in the estuary. It is evident that the Yenisey Estuary was richer by Chl a and plankton biomass in 1993, 1997 and 2000, biological activity was low and comparable in two estuaries in 2001. Primary production in 1993 was higher in the Yenisey Estuary because of unstable meteorological conditions in the Ob Estuary at the time of works were nor favourable for high PP.

Dissolved organic carbon and nutrients

The analyses of DOC behaviour in the mixing zones of the estuaries reveal that DOC demonstrated a linear trend with decrease of the concentration from river to sea. It means that DOC behaviour was conservative independently on the level of biological activity.

Dissolved inorganic nutrients (NO_3, PO_4, and NO_2, NH_4, P_{total} in few expeditions) have shown the complicated behaviour with increase of salinity in the estuaries. In the most cases the nutrient concentrations were decreased with increase of salinity, sometimes they dropped to zero. Significant changes were found at the crossing of the frontal hydrological zones. As a rule, in near bottom waters of high salinity the nutrient concentrations have increased as a result of OM regeneration. A bioactivity of plankton was a little higher in the Yenisey Estuary in 1993, 1997 and 2000 and lower in 1999 (plankton bloom in the Ob Estuary). In agreement with this fact the nitrate and phosphate concentrations were higher in the Ob Estuary in 1993, 1997 and 2000 while nitrate was zero in 1999 in both estuaries.

Dissolved trace elements

Among the elements studied (Fe, Mn, Cu, Zn, Ni, Pb, Cd, Ba, Hg, F, B, Sr) the two metals only (Ni and Cd) have demonstrated the difference in their behaviour in the Ob and Yenisey Estuaries. The behaviour of other elements was similar in both estuaries. Ni was conservative in the Ob and non-conservative in the Yenisey Bay (September 1993) while Cd demonstrated a complex behaviour in both estuaries. Dependencies of Ni and Cd from nutrient concentrations indicated that these two metals were involved into biological cycles. This involvement was more intensive in the Yenisey Estuary.

SPM and particulate elements and components

The data of 1993-2003 show that the SPM concentrations were low and stable in the Yenisey Estuary. At the same time, the sharp peaks of SPM discharge have been detected in the period of spring flood in this estuary. However, the sedimentation processes were more extensive in the Ob Estuary. The ratio of the maximum POC contents in the Ob and Yenisey Estuaries was close to 1 in 1993, 1997 and 2001 when bioactivity of phytoplankton was comparable in two estuaries. However, in 1999, the year of high plankton bloom, this ratio was near 0.8. It means that in the Yenisey Bay the POC content was higher despite lower bioactivity in this estuary. High coefficient of correlation between POC and PN is in agreement that nitrogen is more important for the plankton development than phosphorus.

The data on chemical composition of the Ob and Yenisey SPM show that the major elements are stable (as the ratio Me/Al against salinity) in both estuaries, while some trace elements enriched in the mixing zones due to their involvements to the biological cycles. The level of this involvement is usually more intensive in the Yenisey Estuary. That is in agreement with higher biological activity in this estuary.

The comparison of the intensity of biogeochemical processes in the two estuaries in the integral form in the period between 1993 and 2001 (integral form implicates simultaneous consideration of all parameters together- river discharge, hydrological regime, SPM distribution, concentrations and behaviour of DOC, POC, dissolved and particulate nutrients and chemical elements, level of biological activity of phytoplankton- Chl a concentration, plankton biomass, PP, biomarkers) shows that in the most cases (excluding 1999) the integral intensity of biogeochemical processes was higher in the Yenisey Estuary.

Geochemistry of estuarine bottom sediments

Direct comparison of the Ob and Yenisey Estuarine bottom sediments demonstrates their significant difference in chemical and mineralogical composition. The Yenisey bottom sediments as well as the Yenisey SPM enriched in Ca, Mg, Sr, Ni and some other trace metals as a result of the regularities of geology of the watershed (trap basalts from the Putorana Plateau). The Ob bottom sediments and its SPM enriched in K, Si, Rb, Ba, Pb, Zr as a result of a wide distribution of the materials of shale-like composition in the Western Siberian Lowland in the Ob watershed.

General conclusion

Despite of the existing of significant inter-annual and seasonal variability and several differences in the intensity of biogeochemical processes in the Ob and Yenisey Estuaries the review of all available data for the period between 1993 and 2003 shows that:

1) the differences detected are not very significant in their scale;

2) the general conclusion is that there are more similarities in geochemistry of the two arctic estuaries than the differences between them.

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Annex: Tables 1 - 43

Table 1 Major ion concentrations in the Ob, Yenisey and Lena Rivers.

River	Period of observation	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	CL^-	TDS		Reference
									mg/l	µeq/l	
Ob, Salekhard	1971-1980	19.0	5.1	4.2	3.8	76.3	4.8	9.9	123	3040	Gordeev et al., 1996
	1955-1990	18.6	5.	6.3		78.0	8.5	6.5	121	3244	Tsirkunov et al., 1998
	2001, September	12.0	3.3	6.3	1.1	63.1	5.9	6.1	97.8	2660	"Boris Petrov", 2001
Yenisey, Igarka	1971-1980	15.9	3.3	6.3	1.0	55.2	8.4	9.9	100	2700	Gordeev et al., 1996
	1952-1990	16.5	3.7	6.2		57.3	10.0	9.5	107	2797	Tsirkunov et al., 1998
	2001, August	14.7	4.0	8.4	0.7	62.9	7.1	12.3	110	2920	"Boris Petrov", 2001
Lena, Kiusiur	1980-1990	16.0	4.4	10.0	1.7	52.0	12.3	17.1	119	3230	Gordeev et al., 1996
Global average		13.9	3.3	6.1		47.6	11.9	6.4	89.2	2360	Alekin, 1970
		14.6	4.1	6.3	2.3	58.4	11.2	7.8	105.1	2785	Livingston, 1963
		14.7	3.65	7.2	1.4	53.0	11.5	8.25	99.7	2692	Meybeck, 1979

Table 2 DOC concentration and fluxes in the Ob, Yenisey and Lena Rivers.

River	Year(s)	DOC concentration mg/l	DOC flux, 10^6 t/y	Reference
Ob:				
Salekhard	1959	9.1	2.78	Nesterova, 1960
estuary	1993	7.2-10.1	–	Dai, Martin, 1995
Salekhard-estuary	1997, 1999, 2000	7.7	3.43	Kohler et al., 2003
Yenisey:				
estuary	1993	3.6-4.2	–	Dai, Martin, 1995
estuary		8.5	4.86	Lobbes et al., 2000
estuary	1997, 1999, 2000	8.2	4.86	Kohler et al., 2003
Lena:				
Stolb-delta	1989, 1991	6.6	3.6	Cauwet, Sidorov, 1996
Eurasian Arctic rivers		6.6	19.4	Lobbes et al., 2000 Gordeev, Rachold, 2003
Global average		5.75	215	Meybeck, 1982

Table 3 Dissolved nutrients in the Ob, Yenisey and Lena Rivers (mg/l).

River	Period of observation	N-NO$_3$	N-NH$_4$	DON	TDN	P-PO$_4$	DOP	TDP	SiO$_2$	Reference
Ob, Salekhard	1980-90	0.06	–	–	–	0.065	–	–	2.85	Tsirkhunov et al., 1998
	1975-95	0.098	–	–	–	0.074	–	–	9.6	Gordeev et al., 1996
	1980-92	0.07	–	–	–	–	–	–	2.8	GEMS, 1995
	1997, 1999, 2000	–	–	0.14	–	–	–	–	–	Kohler et al., 2003
Yenisey, Igarka	1980-90	0.02	–	–	–	0.008	–	–	3.0	Tsirkhunov et al., 1998
	1975-95	0.041	–	–	–	0.013	–	–	6.4	Gordeev et al., 1996
	1986-92	0.050	–	–	–	0.015	–	–	3.55	GEMS, 1995
				0.18	–	–	–	–	–	Lobbes et al., 2000
Lena, Kiusiur	1980-90	0.03	–	–	–	0.004	–	–	1.5	Tsirkhunov et al., 1998
	1984-95	0.041	–	0.46	0.54	0.008	0.021	0.029	4.2	Gordeev et al., 1996
	1980-92	0.02	–	–	–	0.009	–	–	1.55	GEMS, 1995
				0.18	–	–	–	–	–	Lara et al., 1998
				0.55	–	–	–	–	–	Cauwet, Sidorov, 1996
Eurasian arctic rivers		0.048	–	–	–	0.025	–	–	5.9	Gordeev et al., 1996
Global average		0.10	0.015	0.26	0.375	0.01	–	0.025	10.4	Meybeck, 1982

Table 4 Hydrochemical characteristics of the Ob (Salekhard) and Yenisey (Dudinka) in June 2001 (Makkaveev and Holmes, 2001).

Parameter	Ob, Section 1, 11.06.00	Ob, Section 2, 11.06.00	Ob, Section 1, 17.06.00	Ob, Section 2, 26.06.00	Yenisey 26.06.00
pH	7.53	7.48	7.34	7.25	7.05
$O_{2\,diss}$ (ml/l)	7.00	6.71	7.17	6.24	6.76
PO_4 (µg/l)	44	35	50	30	16
Si	1.88	1.78	1.84	1.74	2.23
NO_2	1.4	1.9	1.5	1.6	0.6
NO_3	72	117	68	101	10.1
NH_4	39	22	32	25	14

Table 5 Average concentrations of nutrients (µg/l) in the lower reaches of the Ob and Yenisey (Makkaveev and Holmes, 2001).

	Analytical method	Ob, Salekhard			Yenisey, Dudinka		
		$N\text{-}NH_4$	$N\text{-}NO_3$	$P\text{-}PO_4$	$N\text{-}NH_4$	$N\text{-}NO_3$	$P\text{-}PO_4$
Expedition of June 2001	Nesler	1074	66	42	259	15	12
	phenolyt-hydrochloric*	15.8	89.5	39	14	10.1	16
	–"–**	12	–	–	10	–	–
	fluorimetric	11	–	–	10	8.1	–
Multy-annual average of Hydromet (Holmes et al., 2000)		710	90	58	360	30	11

*- modification of P.P. Shirshov Institute of Oceanology RAS,

**- modification of Hydrochemical Institute, Rostov on Don.

Table 6 Compilation of DON concentrations and C/N (molar) ratios in different aquatic environments of the Arctic (Kohler et al., 2003).

Environment	DON (µM N) mean (range)	C/N mean (range)	Salinity range (‰)	Reference
Ob estuary	10 (8-12)	35 (29-44)	13-20	Kohler et al., 2003
Yenisey estuary	13 (8-15)	42 (32-51)	0-19	Kohler et al., 2003
–"–	10	69	1.7	Lobbles et al., 2000
Lena River	33	23	0	Gordeev et al., 1996
–"–	13 (9-28)	48 (30-58)	0	Lara et al., 1998
–"–	39 (6-48)	23 (20-53)	0-18	Cauwet and Sidorov, 1996
Kara Sea	8 (5-10)	26 (19-37)	21-28	Kohler et al., 2003
Laptev Sea	5-6	18-25	30-34	Kattner et al., 1999
Central Arctic	2-12*	9-25**	30-35	Wheeler et al., 1997

* - samples between 40 and 4000 m depth,
** - only samples from upper 100 m

Table 7 Dissolved nutrient concentrations in the Ob and Yenisey Estuaries (µM).

Estuary	S, ‰	N-NO_2	N-NO_3	P-PO_4	P_{org}	P_{tot}	Si
Yenisey							
1993	0	–	0.0-0.4	0.1-0.25	–	–	63.5-83.2
	1-34	–	0.0-9.5	0.2-1.8	–	–	3.0-76.2
2000	0	0.27-0.30	0.06-3.12	0.55-0.65	0.05-0.2	0.65-0.80	57-140
	1-34	0.0-3.82	0.31-6.37	0.10-3.5	0.0-0.4	0.35-3.7	4.5-98.7
2001	0	0.06-0.24	0.08-0.76	0.49-1.55	–	1.23-6.28	63.7-133.1
	1-34	0.30-0.38	0.34-0.76	0.44-1.76	–	0.60-3.75	18.2-80.2
Ob							
1993	0	–	2.0-3.8	1.0-1.9	–	–	24.0-50.5
	1-34	–	0.0-11.4	0.1-2.2	–	–	3.8-57.3
2001	0	0.04-0.32	0.16-0.40	1.02-2.07	–	2.07-3.86	18.2-98.6
	1-34	0.04-0.24	0.08-0.36	0.0-1.02	–	0.07-3.12	17.3-80.7
2002	0	–	–	0.46-3.14	–	–	–
	1-34	–	–	0.82-1.42	–	–	–

Table 8 Concentrations of dissolved trace elements in the Ob, Yenisey and Lena Rivers (µg/l).

River	n	Fe	Mn	Cu	Zn	Ni	Pb	Cd	Cr	Sr	Hg	Reference
Ob	2	25.8	–	2.12	–	1.32	0.014	0.0007	–	–	–	Dai, Martin, 1995
	2	–	–	0.01-0.34	<0.1-0.43	–	0.038-0.106	<0.04-0.053	–	–	–	Kravtsov et al., 1994
	4	–	4.3	3.4	2.5	–	<0.5	<0.05	–	–	–	Leonova et al., 2000
	20	–	11.1	1.0	7.5	–	0.5	0.08	–	–	–	Shvartsev et al., 2000
	10	–	–	2.72	–	2.1	–	0.003	0.28	–	–	Moran, Woods, 1997
	–	8.6-830	0.2-50	0.02-5.9	0.1-46.5	0.03-4.5	0.08-9.6	0.01-0.5	–	–	–	Atlas…, 1999
	8	657	74	2.33	<1	1.83	–	0.0046	0.62	–	–	Expedition of December, 2001
	8	453	<20	–	–	–	–	–	–	63	–	"Boris Petrov", 2001
	1	–	–	–	–	–	–	–	–	70	-	Savenko et al., 2001
Average		145	22	2.33	0.4	1.94	0.014	0.003	0.34	63	0.0006	This work
Yenisey	3	14.3	–	1.62	–	0.54	0.0055	0.0015	–	–	–	Dai, Martin, 1995
	3	–	–	0.01-1.54	0.51-2.0	–	0.018-0.35	<0.04-0.16	–	–	–	Kravtsov et al., 1994
	–	8.2-250	0.2-75	0.1-1.9	0.8-10	0.09-1.05	0.01-2.2	0.01-0.25	–	–	–	Atlas…, 1999
	16	76	<20	–	–	–	–	–	–	133	–	"Boris Petrov", 2001
	4	28	<20	–	–	–	–	–	–	165	–	"Boris Petrov", 2000
	3	–	–	–	–	–	–	–	–	165	–	Savenko et al., 2001
Average		59	–	1.6	1.3	0.5	0.005	0.0015	–	143	0.0003	This work
Lena	2	22.9	–	0.60	0.35	0.30	0.017	0.0015	–	–	–	Martin et al., 1993
	6	35.8	–	0.88	0.45	0.30	0.041	0.006	–	–	–	Guien et al., 1996
		11-200	0.1-8.2	0.1-1.5	0.1-10	0.02-1.1	0.1-0.56	0.02-0.5	–	–	–	Atlas …, 1999
Average		32	–	0.8	0.42	0.3	0.035	0.006	–	–	0.001	Gordeev, 2001
Average for Eurasian rivers		87	–	1.62	0.74	1.28	0.012	0.0034	–	–	0.0005	This work
Global average		40	10	1.5	0.60	0.5	0.03	0.010	–	–	0.005	Martin, Gordeev, 1986 (with corrections)
		66	34	1.48	0.60	0.8	0.079	0.08	0.7	60	-	Guillardet et al., 2004

Table 9 Concentrations of dissolved heavy metals along the Irtysh-Ob River system (µg/l).

River	n	Fe	Mn	Zn	Cu	Ni	Co	Pb	Cd	Cr	Hg	Reference
Upper Irtysh	256-600*	–	37.2	41.4	23.5	–	1.92	16.5	0.72	8.1	–	Panin, 2002
Middle Irtysh (below c. Omsk)	19	20.9	1.2	0.98	2.69	4.6	0.40	0.55	0.052	0.56	0.018	Gordeev, Vlasova, 2002
Tributaries of the Irtysh with brown water	5	364	57	3.3	2.86	7.0	1.2	0.41	0.02	0.42	0.019	–"–
Low Irtysh (at the confluence with the Ob)	4 4	125 –	8.8 –	1.44 –	2.84 3.02	6.2 1.9	0.33 –	0.40 –	0.02 0.0064	0.32 0.18	0.018 –	Gordeev, Vlasova, 2002 Moran, Woods, 1997
Middle Ob	20 3	– –	18.9 –	30.2 –	2.3 2.8	1.0 1.3	0.6 –	0.8 –	0.24 0.006	2.8 0.16	0.022 –	Shvartsev et al., 1996 Moran, Woods, 1997
Low Ob	10 –	– 26	– –	 0.4	2.7 2.1	2.1 1.3	– –	– 0.014	0.003 0.0007	0.28 –	 0.00056	Moran, Woods, 1997 Dai, Martin, 1995
World rivers	–	40	8	0.6	1.5	0.5	0.5	0.03	0.01	1.0	0.005	Martin, Gordeev, 1986

* - unfiltered samples, from n=256 for Cr to n=600 for Zn.

Table 10 **Concentration of dissolved trace elements in the Ob River and Polyi River near Salekhard, December 2001.**

Station	Horizon, m	Fe	Mn	Cu	Zn	Ni	Co	Cr	Cd	As
Ob, 1	0	1268	143	2.14	<1	1.88	0.047	0.57	0.012	0.73
1	8	361	126	3.15	<1	1.66	0.049	0.49	0.0074	0.71
2	0	616	69	2.80	<1	0.95	0.040	0.81	0.011	0.60
3	0	840	65	2.55	<1	1.46	0.027	0.51	0.0051	0.68
4	0	639	62	1.54	<1	–	0.045	0.44	0.0018	0.56
5	0	1244	80	1.60	<1	3.21	0.046	0.84	0.0042	0.95
6	0	992	84	2.60	<1	–	0.043	0.68	0.0020	0.62
7	0	493	85	2.27	<1	–	0.041	0.43	0.0071	0.42
Polyi, 1	0	557	855	1.41	<1	2.16	0.15	0.44	0.0040	0.40
2	0	676	873	0.57	<1	1.41	0.12	0.56	0.0075	0.58

Table 11 **Clay minerals in SPM and bottom sediments in the Ob and Yenisey Estuaries (in % of their sum) after the results of the 28-th cruise of the R/V "Academic Boris Petrov", 1997 (Mullerand Stein, 1999).**

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

Table 12 POC and TOC concentrations in the Ob, Yenisey and Lena Rivers.

River	n	POC, mg/l	POC, %	TOC, mg/l	$\frac{\text{POC}}{\text{TOC}}$ %	Reference
Ob:						
Salekhard, 1959	–	0.9	2.0	10.0	9.0	Nesterova, 1960
Multi-annual average	–	–	–	7.1	–	Smirnov et al., 1988
	–	–	–	8.8	–	Telang et al,. 1991
Salekhard, December 2001	8	0.7-1.35 av. 0.96	5.1-21.9 av. 12.8	–	–	This work
Salekhard-Pur-Taz, September 2002	21	0.09-0.71 av.0.27	2.1-6.8 av. 4.2	–	–	This work
Estuary, September 1993	5	0.19-2.1 av. 0.95	2.6-3.4 av. 2.9	–	–	Gordeev et al., 1995
Yenisey:						
Multi-annual average		–	–	7.4	–	Maltseva et al., 1987
		–	–	7.4	–	Telang et al., 1991
		0.3		8.8	3.4	Lobbes et al., 2000
Estuary, September 1993	3	0.13-0.73 av. 0.47	4.3-5.1 av. 4.7	–	–	Gordeev et al., 1995
Lena:						
Stolb-delta 1989, 1991		1.1	4.1	7.7	14.3	Cauwet, Sidorov, 1996
		–	–	9.5	–	Telang et al., 1991
Eurasian arctic rivers		1.3	3.6	8.8	14.8	Gordeev, Rachold, 2003
Global average		4.8	1.0	10.55	45.9	Meybeck, 1982

Table 13 POC concentrations in the Ob River near Salekhard, December 2001.

Station	Horizon, m	SPM, mg/l	POC mg/l	POC %
Ob:				
1	0	6.2	1.35	21.9
1	8	22.0	1.12	5.1
2	0	8.0	1.05	13.0
3	0	7.0	0.83	11.9
4	0	8.4	0.70	8.2
5	0	5.1	0.92	17.8
6	0	5.8	0.88	15.1
7	0	9.4	0.87	9.3
average		7.1	0.96	12.8
Polyi:				
1	0	11.5	1.97	17.2
2	0	15.3	2.07	13.5
average		13.4	2.02	15.3

Table 14 POC concentrations in the Ob River and Estuary, September 2002.

Station	SPM, mg/l	POC, mg/l	POC, %
02	1.4	0.07	5.2
03	3.3	0.13	3.8
04	3.6	0.15	4.2
05	10.5	0.40	3.7
06-1	7.0	0.48	6.8
06-2	15.4	0.65	4.2
07	9.9	0.55	5.6
08	10.5	0.45	4.3
09-1	7.7	0.41	5.3
09-2	3.9	0.35	9.0
10	3.7	0.42	11.3
12	4.2	0.62	14.7
13	9.6	0.55	5.8
14	2.6	0.14	4.8
15	1.9	0.09	4.9
16	18.7	0.71	3.8
17	5.2	0.11	2.1
19	9.8	0.36	3.1
21	12.5	0.48	3.3
22	4.4	0.21	4.9
23	9.5	0.30	3.2
average*	7.9	0.27	4.2

*- Sts. 9, 10, 12, 13 do not include to average because they were sampled in the Taz Estuary.

Table 15 Particulate forms of P (PPh) and N (PN) in the Yenisey River.

River	n	PPh, mg/l	PPh, %	PN mg/l	PN %	Reference
Ob:						
Salekhard, December 2001	7	0.031-0.063 av. 0.047	0.56-0.88 av. 0.67	–	–	This work
Polyi River,	2	0.25-0.31	2.0-2.3	–	–	–"–
Salekhard - - Pur - Taz, September 2002	10	0.011-0.040 av. 0.023	0.20-0.40 av. 0.29	–	–	–"–
BP-1997 S=2.5-3.3‰	3	0.01-0.018 av. 0.013	0.20-0.38 av. 0.28	–	–	Lukashin et al., (1999)
BP-1999 S=0-1.8-2.9‰	2	–	–	0.12	1.51-1.59 av. 1.55	
BP-2001 S=0-1.2‰	6	0.039-0.090 av. 0.06	0.34-0.72 av. 0.48	0.035-0.14 av. 0.08	0.28-0.87 av. 0.68	Gaye et al., (personal communication)
Yenisey:						
BP-1997 S=1.2-1.3‰	3	0.008-0.01 av. 0.009	0.17-0.23 av. 0.20	–	–	Lukashin et al., (1999)
BP-2000						
S=0-0.5‰	7	0.01-0.018 av. 0.012	0.19-0.31 av. 0.27			
S=0-0.6‰	5			0.04-0.07 av. 0.05	0.78-1.25 av. 1.12	Gaye et al., (personal communication)
BP-2001						
S=0-1.2‰	8	0.003-0.021 av. 0.012	0.21-0.50 av. 0.37			
S=0-1‰	12			0.042-0.066 av. 0.053	0.87-3.07 av. 1.41	Gaye et al., (personal communication)

Table 16 Major elements composition of the Ob, Yenisey and Lena suspended matter in (%).

River	n	Si	Al	Fe	Mg	Ca	K	Na	Ti	Mn	P	Reference
Ob	3	25.1	6.8	4.6	0.94	1.06	2.79	1.6	0.43	0.12	–	Morozov et al., 1974
	1	26.1	7.3	6.3	1.19	0.96	1.63	0.73	0.41	0.35	0.16	Savenko et al., 2004
	5	24.5	6.9	6.0	2.20	0.83	1.60	0.71	–	0.29	–	Gordeev et al., 1995
	9	–	4.5	8.6	0.77	1.25	0.96	0.37	0.26	0.27	0.44	"Boris Petrov", 2001
	8	–	4.7	11.55	0.67	1.89	0.73	0.36	0.81	0.13	0.65	Expedition, December 2001
	10	–	7.2	7.3	1.09	1.25	1.49	0.68	0.46	0.23	0.29	Expedition, September 2002
Average	26	24.9*	5.9	8.0	0.93	1.28	1.34	0.63	0.46	0.22	0.41	This work
Polyi	2	–	1.1	31.0	0.27	1.15	0.20	0.14	0.29	0.18	2.10	Expedition, December 2001
Yenisey	1	22.5	6.8	6.5	1.79	1.83	1.32	0.57	0.16	0.15	0.12	Savenko et al., 2004
	3	22.8	6.5	5.9	1.89	1.76	1.34	1.01	–	0.19	–	Gordeev et al., 1995
	8	–	2.75	3.6	0.75	1.08	0.61	0.37	0.19	0.26	0.33	"Boris Petrov", 2001
	7	–	5.7	5.2	1.58	1.65	1.09	0.74	0.42	0.38	0.27	Beeskow, Rachold, 2003
Average	12	22.7**	4.7	4.7	1.29	1.43	0.91	0.62	0.29	0.28	0.29	This work
Lena	5	–	6.7	3.3	1.27	0.42	2.36	1.78	–	0.12	–	Gordeev, Shevchenko, 1995
	31	–	7.1	3.8	1.38	1.47	2.12	1.34	0.36	0.16	–	Rachold, 1999
Average	36		7.0	3.7	1.36	1.32	2.15	1.40	0.36	0.16	–	This work
Eurasian arctic rivers		23.6	5.8	5.25	1.23	1.35	1.43	0.89	0.32	0.22	0.34	This work
Global average		25.5	8.3	5.1	1.25	2.50	1.5	1.0	0.40	0.11	0.11	Gordeev, 1983

* - n=9
** - n=4

Table 17 Trace element content in the Ob, Yenisey and Lena suspended matter (µg/g)/

River	n	Cu	Zn	Ni	Co	Pb	Cd	Cr	Sr	Ba	V	Zr	As	Hg	Reference
Ob	6	50	115	38	19	16	0.53	99	–	–	–	–	–	–	Gordeev et al., 1995
	1	34	115	60	25	24	–	111	125	480	141	130	9.6	–	Savenko et al., 2004
	9	37	209	48	20	34	0.41	100	–	424	147	83	38	–	"Boris Petrov", 2001
	7	66	670	–	–	47	2.2	82	149	–	106	101	61	–	Expedition, December 2001
	10	41	615	63	30	38	0.70	106	146	190	136	145	27	–	Expedition, September 2002
															Shevchenko et al., 19….
Ob - Irtysh		26	–	29	–	15	0.58	50	–	–	–	–	–	–	Moran, Woods, 1997
Average		46	263	52	24	34	0.55	108	145	310	134	118	36	0.05	This work
Yenisey	3	144	220	77	23	30	2.2	130	–	–	–	–	–	–	Gordeev et al., 1995
	1	–	–	–	28	–	1.18	–	226	431	153	130	8.8	–	Savenko et al., 2004
	7	81	205	74	30	32	0.56	–	190	385	138	–	11.6	–	Beeskow, Rachold, 2003
	3	–	–	–	–	–	—	-	–	–	–	–	–	0.05	Goquery et al., 1995
Average	11	100	209	75	24	31	1.06	130	194	340	140	130	11.2	0.05	This work
Lena	2	28	143	31	–	23	–-	–	–	–	–	–	–	–	Martin et al., 1993
	6	28	160	34	13	36	0.25	–	–	–	–	–	–	–	Gordeev, Shevchenko, 1995
	31	35	141	53	18	24	0.65	–	194	718	97	132	9.1	–	Rachold, 1996
	5	42	185	42	–	42	0.96	–	–	–	–	–	–	–	Nolting et al., 1996
Average	44	34	148	48	17	27	0.63	–	194	718	97	132	9	–	This work
Eurasian arctic average		46	212	53	21	29	0.69	121	176	570	125	173	19	0.05	This work
Global average		80	250	84	20	35	0.7	130	150	600	130	200	5	–	Martin, Gordeev, 1986 (with corrections)

Table 18 Rare Earth Elements in SPM of the Ob and Yenisey Rivers (µg/g).

River	Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Ln	Reference
Yenisey	Average for 7 samples	27	54	6.4	25	5.9	1.5	5.8	0.74	5.6	1.0	2.9	0.49	2.6	0.68	Beeskow, Rachold, 2003
	Y1*	15	26	(2.1)**	6.2	1.3	0.35	(1.7)	0.28	(1.8)	(0.43)	(1.3)	(0.22)	1.3	0.24	Gordeev et al., 1995
	Y2	14	25	(2.5)	9.2	2.3	0.60	(3.2)	0.66	(3.1)	(0.72)	(2.1)	(0.33)	1.95	0.34	
Ob	O1	21	32	(3.0)	9.5	1.7	0.86	(3.3)	0.52	(3.1)	(0.70)	(2.0)	(0.30)	1.75	0.29	Gordeev et al., 1995
	O2	15.7	30.4	(3.3)	12.9	3.2	0.70	(3.7)	0.58	(3.6)	(0.84)	(2.5)	(0.39)	2.2	0.40	
Global average		45	95	(8)	35	7	1.5	5	1.0	(1)	(1)	(3)	(0.4)	3.5	0.5	Martin, Meybeck, 1979
Upper continental crust		31	63	7.1	27	4.7	1.0	4.0	0.7	3.9	0.83	2.3	0.30	2.0	0.31	Rudnick, Gao, 2004

* Y1 and Y2 - combined SPM samples (salinity 0.5-1.9 ‰ and 9-22 ‰);
O1 and O2 - combined SPM samples (salinity 0 ‰ and 10-23‰)
** indirectly estimated magnitudes.

Talbe 19 Average chemical composition of SPM in (1) the middle Irtysh, (2) intermediate Irtysh waters and (3) brown water tributaries and Ob River (Gordeev et al., 2004).

Element, component	(1) Middle Irtysh (Sts. 1-5, 7, 9 11, 12)	(2) Intermediate water (Sts.10, 14, 16)	(3) Brown water tributaries (Sts. 8, 13, 15, 17, 1 8)	(4) Representative lower Irtysh (Sts. 14, 16)	(3)/(1) ratio
SPM	18.1	15.2	13.1	16.8	0.57
POC	1.09	0.98	1.22	1.07	1.67
Al_2O_3	13.20	11.50	7.62	11.50	0.58
Fe_2O_3	6.27	10.11	15.53	10.6	2.55
CaO	1.49	2.10	2.53	1.75	1.70
K_2O	1.85	1.55	0.98	1.52	0.54
MgO	1.77	1.66	1.15	1.59	0.65
MnO	0.30	0.43	0.29	0.41	0.80
Na_2O	0.68	0.49	0.38	0.49	0.60
P_2O_5	0.55	1.23	1.94	1.10	3.52
TiO_2	0.59	0.56	0.38	0.55	0.65
As	29	52	67	52	2.39
Ba	457	534	548	480	1.18
Cd	1.88	1.32	1.07	1.33	0.58
Co	25	32	–	≤32	–
Cr	121	129	126	125	1.05
Cu	47	42	45	42	1.00
Ni	60	61	52	62	0.87
Pb	38	39	36	39	1.00
Sr	125	174	155	145	1.36
V	115	154	131	162	1.00
Zn	195	196	175	209	0.92
Zr	136	116	88	115	0.65

[a] The representative composition of the Irtysh River (4) at the confluence with the Ob River is
shown as well (SPM and POC in mg/l, major elements in weight % and trace elements in µ/g
– = not determined.

Table 20 Average composition of the West Siberia lowland peat (Inisheva and Tsibukova, 1999) and SPM of brown-water rivers as well as their ratios for the investigated chemical elements in weight %, trace elements in μg/g, - =no data) (Gordeev et al., 2004).

Element/oxide	SPM of brown waters	Upper layer peat (UP)	Low-lying peat (LP)	UP / SPM_{bw}	LP / SPM_{bw}
Fe_2O_3	15.53	0.28	1.28	0.018	0.082
MnO	0.29	0.012	0.077	0.041	0.26
CaO	2.50	0.40	5.90	0.16	2.36
Na_2O	0.38	0.031	0.065	0.081	0.17
As	67	–	–	–	–
Ba	548	47	275	0.085	0.50
Cd	1.07	–	–	–	–
Co	32	1.1	2.4	0.034	0.075
Cr	126	7.6	12.3	0.06	0.10
Cu	45	7.0	10.8	0.15	0.24
Pb	36	3.1	4.9	0.086	0.13
Sr	156	80	338	0.51	2.16
Zn	175	6.6	15.5	0.038	0.088
V	131	2.1	11.7	0.015	0.089

Table 21 Average concentrations of dissolved elements (in μg/l) in the middle Irtysh before (1) and after (2) the inflow of brown waters, brown water tributaries (3), and the lower Irtysh River (4) at the confluence with the Ob River (Gordeev et al., 2004).

Element, component	(1) Middle Irtysh, before inflow of brown waters (Sts. 1-5, 7)	(2) Middle Irtysh, after inflow of brown waters (Sts. 9, 11-12)	(3) Brown water tributaries (Sts. 8, 13, 15, 17, 18)	(4) Respresentative lower Irtysh (Sts. 14, 16)	(3)/(1) ratio
Fe	20.9	228.2	364	110	17.4
Mn	1.1	23.5	57	4.0	51.8
Cu	2.69	3.20	2.90	3.0	1.07
Zn	0.97	1.5	2.5	1.6	2.58
Ni	4.6	5.5	7.0	6.2	1.520
Pb	0.55	0.43	0.41	0.4	0.75
Cd	0.052	0.020	0.020	0.02	0.38
Cr	0.56	0.49	0.42	0.32	0.75
Hg	0.018	0.011	0.019	0.018	1.05
Ca	27.400	–	30.000	–	1.09
Sr	0.22	–	0.24	–	1.1
PO_4	48	–	90	–	1.9

Fe-Hg data are taken from Gordeev and Vlasova (2002); Ca, Sr and PO_4 data from Sazonova and Shvartsev (2002) [in Sazonova and Shvartsev (2002) water samples on Sta. 9, 11-12, 14 and 16 were not obtained].

Table 22 Multi-annual dissolved major-ion export to the Arctic Ocean (in 10^6t/y). TDS-total dissolved salts, DT-dissolved transport.

River	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	TDS	DT t/km^2
Ob	7.67	2.06	1.70	1.53	30.8	1.94	4.00	49.7	19.5
Yenisey	9.86	2.05	3.90	0.62	34.2	5.20	6.14	62.0	23.9
Lena	8.42	2.32	5.26	0.88	27.3	6.46	8.98	59.6	23.4
Total Eurasian Arctic	45.5	10.7	13.8	3.44	143.5	29.8	21.5	268.2	20.5

Table 23 DOC, POC and TOC fluxes for the Ob, Yenisey Rivers (Kohler et al., 2003).

	Discharge, km^3	DOC, mg/l	DOC export, 10^6 t
Ob			
Nov. - Apr.	82.8	3.6	0.30
May	39.5	9.0	0.36
June	90.4	10.8	0.98
July	79.6	9.0	0.72
August	53.5	7.7	0.41
Sept.	32.4	6.5	0.21
Oct.	27.9	5.0	0.14
annual	406	DOC POC TOC	3.12×10^6 t 0.31×10^6 t 3.43×10^6 t
Yenisey			
Nov. - Apr.	132.5	3.6	0.48
May	77.4	8.5	0.66
June	201.8	10.8	2.18
July	64.3	9.6	0.62
August	41.9	9.0	0.38
Sept.	41.3	8.3	0.34
Oct.	34.9	5.7	0.20
annual	594	DOC POC TOC	4.86×10^6 t 0.17×10^6 t 5.03×10^6 t

Table 24 Annual nutrient fluxes for the Ob, Yenisey and Lena Rivers (10^3 t/y).

River	N-NO_3	DON	TDN	PON	P-PO_4	DOP	TDP	POP	Reference
Ob	34.8	–	–	–	23.5	–	–	–	Holmes et al., 2000
	42.0	–	–	–	32.0	–	–	–	Gordeev, 2000
	–	56.5*	–	12-40**	–	–	–	5-16**	This work
Yenisey	18.4	–	–	–	6.2	–	–	–	Holmes et al., 2000
	25.4	–	–	–	8.1	22.3	30.4	–	Gordeev, 2000
	–	111.6*	–	22**	–	–	–	8**	This work
Lena	19.5	–	–	–	3.5	–	–	–	Holmes et al., 2000
	21.7	243	286	–	4.2	11	15.2	–	Gordeev, 2000
Total Eurasian Arctic	172.2	–	–	–	47.0	–	–	–	Gordeev, 2000

*- Kohler et al., 2003

** - assessed values for PON and POP calculated from POC/PON = 8.5 and POC/POP = 22 (Meybeck, 1982).

Table 25 Fluxes of dissolved and particulate major elements in the Ob, Yenisey and Lena Rivers (10^3t/y). F,%= $Q_{diss.}/Q_{diss.}+Q_{diss.}$

River		Si	Al	Fe	Ca	Mg	Na	K	Ti
Ob	diss.	1500	–	58.5	7676	2060	1697	1535	–
	part.	3860	915	1240	200	144	97	208	71
	∑	5360	–	1298	7876	2204	1794	1743	–
	F, %	28.0	–	4.6	97.5	93.4	94.6	88.0	–
Yenisey	diss.	1710	–	59.5	9850	2050	3900	620	–
	part.	1070	220	220	67	60	29	43	13
	∑	2780	–	280	9917	2120	3930	663	–
	F, %	61.5	–	21.2	99.3	97.1	99.3	93.5	–
Lena	diss.	1030	–	17	8450	2310	5250	890	–
	part.	5160	1450	766	273	280	290	445	76
	∑	6190	–	783	8723	2590	5540	1335	–
	F, %	16.6	–	2.1	96.8	89.0	94.8	66.7	–
Total Eurasian Arctic	diss.	7340	–	257	45980	10770	13320	4250	–
	part.	31300	5930	5365	1380	1256	910	1460	367
	∑	38640	–	5622	47360	12026	14230	5710	–
	F, %	19.0	–	4.6	97.1	89.6	93.6	74.4	–

Table 26-I. Concentrations of total suspended matter, POC, PO_4, NO_3, Si in the Ob and Yenisey Estuaries – 49th cruise of the R/V "Dmitry Mendeleev" – 1993(*

Station depth (m)	Sampling depth (m)	TSM (mg/l)	POC (%)	POC (mg/l)	$P-PO_4$ (µm)	$N-NO_3$ (µm)	$Si-SiO_3$ (µm)	S ‰
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Yenisey								
4400	0	0.25	40.8	0.102	0.48	0.18	6.7	24.45
35	7	0.28	–	–	0.37	0.14	6.4	25.09
	15	0.38	25.0	0.095	1.60	0.12	3.6	27.36
	20	0.53	–	–	0.68	0.27	3.0	
	25	0.40	–	–	0.76	2.4	6.0	29.08
	32	0.94	6.9	0.065	1.71	7.4	17.4	30.97
4401	0	1.05	15.5	1.163	0.29	0.00	37.3	13.57
34	3	0.85	–	–	0.47	0.39	27.8	18.71
	8	0.76	–	–	0.76	0.72	10.6	26.30
	15	0.45	25.5	0.115	1.56	0.87	12.6	32.29
	20	0.65	–	–	1.62	7.1	16.9	33.21
	25	1.21	–	–	1.73	8.1	16.8	33.62
	30	1.55	5.8	0.089	1.73	8.0	16.9	33.66
4402	0	1.36	25.9	0.285	0.18	0.00	44.0	16.40
37	5	1.26	–	–	0.68	0.48	27.1	19.40
	10	0.67	17.5	0.128	0.44	0.05	10.2	25.95
	15	0.59	–	–	0.85	2.5	13.2	32.30
	20	0.83	7.3	0.11	1.32	5.9	16.6	33.05
	25	1.21	–	–	1.14	4.4	18.3]	33.31
	30	2.31	5.6	0.153	0.79	1.1	19.3	33.36
4403	0	1.17	27.5	0.322	0.35	0.30	–	11.51
23	5	1.89	16.6	0.315	0.91	2.4	–	26.67
	10	1.03	10.9	0.113	1.42	5.6	–	32.27
	15	4.45	5.4	0.24	1.73	7.2	–	32.73
4404	0	1.79	14.8	0.267	0.19	0.40	48.7	10.20
14	4	1.53	21.5	0.329	0.19	0.40	49.4	10.29
	8	1.80	17.3	0.311	0.34	1.45	35.8	17.47
	12	2.09	8.2	0.171	0.93	4.1	24.5	27.61
4405	0	2.60	11.2	0.291	0.16	–	74.2	0.97
16	5	3.92	9.1	0.356	0.14	–	75.6	0.97
	10	3.22	11.8	0.379	0.19	–	76.2	0.95
4406	0	8.77	9.3	0.82	0.16	0.38	63.5	0.12
17	5	14.05	5.4	0.763	0.21	0.32	64.3	0.10
	10	8.10	11.4	0.924	0.24	0.38	67.9	0.35
4407	0	3.16	9.6	0.305	–	–	–	0.11
20	5	5.00	8.3	0.415	–	–	–	0.11
	10	3.76	8.8	0.335	–	–	–	0.115
	15	2.88	12.1	0.35	–	–	–	3.39
4408	0	4.34	9.3	0.404	0.20	0.13	82.0	0.046
17	4	2.94	–	–	0.20	0.00	83.2	0.046
	7	2.62	12.6	0.331	0.29	0.28	82.6	0.047
	13	5.13	4.7	0.244	0.32	11.6	76.2	0.047
4409	0	–	–	–	0.19	0.20	77.6	0.30
15	5	–	–	–	0.21	0.25	80.0	0.30
	12	–	–	–	1.11	4.2	69.3	11.89

Table 26-I continued

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
4410	0	3.04	13.0	0.394	0.09	0.10	75.3	0.85
21	5	2.71	13.9	0.377	0.10	0.20	65.4	0.92
	10	4.40	8.0	0.352	0.22	3.3	67.1	9.66
	14	10.34	5.4	0.563	0.61	7.7	50.8	22.18
	17	29.06	13.8	1.102	0.76	8.1	48.4	24.21
4411	0	1.49	21.4	0.319	–	–	–	1.71
29	5	2.58	–	–	–	–	–	1.72
	10	2.56	18.4	0.472	–	–	–	2.12
	20	9.84	15.6	0.552	–	–	–	25.63
4412	0	1.68	15.7	0.264	0.10	0.16	67.9	1.10
21	5	4.18	–	–	0.10	0.07	67.9	1.09
	10	1.77	5.2	0.25	0.13	0.80	66.3	3.48
	16	5.47	4.6	0.25	0.74	7.2	45.6	20.93
	19	16.15	2.7	0.44	0.77	8.6	40.5	24.82
4413	0	8.8	3.5	0.31	0.27	2.2	55.6	8.16
13	5	8.12	–	–	2.55	5.2	38.8	18.96
	8	–	–	–	1.47	8.1	23.1	29.73
	10	21.16	2.8	0.60	1.45	8.5	23.1	29.88
4398	0	0.23	37.4	0.086	0.55	0.06	9.6	23.68
55	6	0.23	–	–	0.40	0.06	8.6	24.17
	12	0.24	73	0.175	0.45	0.02	6.4	25.49
	15	0.41	–	–	2.30	0.75	10.5	29.29
	20	0.17	73.5	0.125	0.97	1.50	11.3	30.99
	35	0.27	71.1	0.192	1.35	7.0	9.8	33.67
	45	0.35	–	–	1.45	8.0	13.8	33.97
	52	0.50	15.4	0.077	1.21	7.9	14.0	33.92
4399	0	0.28	–	–	0.23	0.08	10.3	22.47
41	5	0.53	23.7	0.123	0.44	0.07	10.1	22.86
	10	0.31	17.7	0.055	0.61	0.15	9.2	24.52
	20	0.42	20.4	0.086	1.22	4.3	12.9	31.86
	30	0.73	10.8	0.079	1.61	8.5	16.0	33.81
Ob	0	0.59	26.6	0.157	0.14	0.02	22.2	14.88
4397	5	0.84	–	–	0.16	0.00	20.5	15.47
150	10	0.75	18.9	0.142	0.21	0.11	16.8	17.39
	20	0.21	–	–	0.56	0.15	4.7	31.89
	40	–	–	–	0.89	4.2	4.3	33.57
	50	0.19	17.9	0.034	0.98	4.7	4.5	33.70
	80	0.24	13.3	0.032	1.21	6.4	5.1	34.15
	100	0.13	31.5	0.041	–	–	–	34.24
	120	0.31	10.0	0.031	–	–	–	34.33
4396	0	0.35	31.4	0.11	0.10	0.00	16.4	19.99
34	5	0.29	–	–	0.15	0.02	15.2	20.59
	10	0.31	32.2	0.10	0.26	0.17	16.2	24.34
	15	0.10	45.0	0.045	0.35	1.7	16.6	27.73
	20	0.98	–	–	0.45	3.1	19.0	29.26
	25	0.24	–	–	0.98	6.0	18.6	32.28
	32	1.03	10.0	0.105	1.13	6.7	19.6	32.93

Table 26-I continued

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
4395	0	0.46	25.8	0.119	0.16	0.24	8.4	24.34
31	3	0.33	34.8	0.115	0.16	0.24	8.0	24.33
	8	0.36	32.2	0.116	0.47	0.44	9.0	26.78
	15	0.24	27.9	0.067	0.65	2.3	16.2	29.33
	17	0.23	34.8	0.080	1.31	3.4	17.6	29.51
	23	8.43	5.9	0.495	1.69	5.8	23.6	31.54
	28	0.71	7.3	0.709	1.89	7.3	29.4	32.00
4414	0	4.40	5.5	0.24	0.65	2.20	33.4	15.04
25	4	0.62	14.7	0.091	0.46	1.00	20.0	19.59
	7	–	–	–	0.41	0.40	6.1	26.98
	10	1.0	9.0	0.09	0.45	0.40	6.6	26.26
	15	0.53	–	–	1.12	4.45	20.8	30.24
	20	25.48	4.3	1.09	1.20	9.9	29.2	32.31
4415	0	4.04	11.5	0.465	0.95	3.45	35.1	8.19
24	5	3.28	7.1	0.234	1.62	9.60	29.0	21.90
	10	3.90	11.4	0.446	1.65	9.00	29.7	21.11
	17	5.48	4.3	0.237	2.18	11.3	30.0	31.39
4416	0	6.73	10.7	0.72	0.82	2.63	29.0	1.29
19	3	13.75	6.5	0.832	1.35	2.68	29.2	1.29
	6	11.60	7.6	0.888	1.30	2.58	30.4	2.08
	10	6.16	7.2	0.446	1.35	6.40	49.6	11.33
	12	4.85	8.6	0.42	1.28	6.80	51.4	11.98
	16	6.29	8.7	0.55	1.30	8.50	57.3	17.30
4417	0	10.34	9.9	1.026	0.97	2.15	24.0	0.0
24	10	12.00	10.1	1.218	0.81	2.10	24.0	0.0
	25	11.70	9.1	1.07	1.00	2.05	24.0	0.0
4418	0	80.70	7.2	5.79	1.74	3.35	50.5	0.0
13	4	115.3	4.6	5.26	1.05	3.20	49.5	0.0
	8	72.70	5.8	4.25	1.87	3.70	49.0	0.0
4419	0	16.05	5.4	0.868	1.17	2.90	2.80	1.06
27	5	16.93	6.8	1.155	–	–	–	1.07
	10	20.80	4.7	0.986	1.17	2.85	28.0	1.07
	15	16.20	–	–	–	–	–	1.07
	20	–	–	–	1.60	3.05	28.3	1.07
	24	16.70	5.9	0.99	1.13	4.70	37.4	4.76
4420	0	11.85	4.4	0.523	0.83	2.9	38.0	4.86
17	5	10.00	6.7	0.674	0.79	3.1	38.0	6.07
	11	7.30	9.3	0.679	0.71	3.4	39.0	7.25
	15	12.43	4.9	0.611	0.90	5.2	42.0	19.98
4421	0	4.83	7.4	0.357	1.16	5.4	36.0	16.85
13	4	5.28	7.3	0.392	1.46	6.6	34.5	17.65
	7	36.12	3.0	1.073	1.41	8.7	31.5	29.52
	10	51.88	2.6	1.36	1.59	9.1	31.0	29.72

(* TDC, POC(%), POC(mg/l) – Shevchenko et al., 1997;
P-PO_4, N-NO_3, Si-SiO_3 – Makkaveev and Stunjhas, 1994

Table 26-II. Nutrient concentrations (µM) in the Ob and Yenisey Estuaries – BP-1999 (Sukhoruk and Tokarev, 2000).

Station	Sampling depth, m	P-PO_4	N-NO_3	Si-SiO_3	S, ‰
		Yenisey			
6	2	1.60	<0.02	10.49	2.6
8	2	0.78	0.08	21.35	4.7
	12	0.78	0.06	12.91	5.2
	15	0.41	<0.02	29.80	7.2
11	3	0.03	0.25	23.16	7.4
	7	0.03	<0.02	28.59	7.9
	36	1.03	0.06	14.72	33.2
13	2	0.41	<0.02	21.96	8.8
	8	0.41	<0.02	31.61	10.6
	15	0.78	<0.02	26.78	25.5
	32	1.54	<0.02	22.56	33.2
30	2	1.16	0.46	8.08	5.3
	11	1.03	0.67	6.87	5.7
31	3	0.53	<0.02	13.51	4.7
	11	1.16	0.25	21.96	4.9
	16	2.42	<0.02	38.25	29.6
32	2.5	0.41	0.50	7.47	5.9
	16	1.41	1.68	19.54	8.8
	25	1.79	<0.02	20.75	32.0
35	3	0.28	1.55	17.73	12.7
	8.5	0.66	2.44	23.77	21.5
	32.5	1.41	0.29	20.15	33.2
		Ob			
1	1.5	0.41	0.04	39.15	6.0
	6	0.53	0.23	38.57	12.0
	24	0.66	0.13	14.38	30.0
17	2	4.55	<0.02	12.91	8.3
	7	1.91	<0.02	16.53	21.2
	16	4.43	<0.02	24.37	30.5
18	2	1.22	<0.02	4.76	1.8
	9	1.22	<0.02	5.24	11.7
	12	0.91	0.32	28.72	26.0
20	3	1.41	0.06	8.08	2.9
	12	3.80	0.21	29.80	27.8
21	3	0.78	0.04	16.53	7.2
	10	2.92	0.65	24.97	21.3
	15	4.05	0.29	27.99	30.0
25	2	0.28	<0.02	20.15	9.2
	9	0.28	0.17	31.61	14.9
	15	2.29	0.05	38.25	29.3
	24	0.66	0.38	6.31	32.4
37	3	0.34	0.38	7.47	9.9
	8	0.66	0.34	12.30	18.9
	29	1.54	0.08	15.32	32.6

Table 26-III Concentrations of total suspended matter, POC, N_{tot}, C/N, in the Ob and Yenisey Estuaries – BP-1999 (Haike et al., raw data).

Station	Sampling depth, m	TSM, mg/l	POC, %	POC, mg/l	N_{tot} %	N mg/l	C/N	S, ‰
1	2	3	4	5	6	7	8	9
Yenisey								
2	1.5	3.68	22.27	0.82	2.31	0.08	11.21	5.5
2	1.3	4.0	23.22	0.93	2.41	0.10	11.21	6.3
2	26	0.44	–	–	–	–	–	30
3	0	1.5	22.59	0.34	2.73	0.04	9.64	6
3	8	1.56	24.42	0.38	2.74	0.04	10.40	9.2
3	28	0.46	–	–	–	–	–	30.6
3	29	0.99	9.71	0.096	0.77	0.007	14.7	32.8
6	0	217.94	2.95	6.44	0.26	0.56	13.3	2.6
8	3	2.81	10.00	0.28	1.22	0.03	9.52	4.7
8	12	2.79	11.17	0.31	1.38	0.04	9.42	5.2
8	15	32.55	3.18	1.03	0.31	0.10	11.91	7.2
11	0	1.26	26.72	0.34	3.96	0.05	7.85	7.4
11	7	1.27	20.27	0.26	2.64	0.03	8.93	7.9
11	30	4.77	4.09	0.19	0.42	0.02	11.32	33.2
13	0	1.71	30.07	0.51	3.90	0.07	8.97	8.8
13	8	1.32	30.24	0.40	3.97	0.05	8.88	10.6
13	15	0.45	–	–	–	–	–	25.5
13	31	2.82	5.09	0.14	0.63	0.02	9.41	33.2
30	0	15.25	4.10	0.63	0.43	0.07	11.04	5.3
30	10	13.19	4.38	0.58	0.42	0.05	12.14	5.7
31	0	7.31	5.03	0.37	0.57	0.04	10.30	4.7
31	11	7.38	5.62	0.41	0.58	0.04	11.30	4.9
31	15	37.3	3.17	1.18	0.31	0.11	12.02	29.6
32	0	5.09	6.47	0.33	0.73	0.04	10.27	5.9
32	16	8.14	4.42	0.36	0.47	0.04	11.00	8.8
32	25	13.79	3.50	0.48	0.37	0.05	10.88	32.0
35	0	2.14	25.44	0.54	3.01	0.06	9.83	12.7
35	8.5	1.08	25.41	0.27	1.76	0.02	16.78	21.5
35	30	4.16	4.58	0.19	0.47	0.02	14.39	33.2
Ob								
1	0	2.88	23.96	0.69	2.87	0.08	9.72	6
1	6	4.11	27.93	1.15	3.15	0.13	10.33	12
1	24	0.40	–	–	–	–	–	30
17	0	29.49	3.52	1.04	0.36	0.11	11.23	8.3
17	6	14.81	4.51	0.67	0.49	0.07	10.72	21.2
17	14	33.68	3.07	1.04	0.34	0.11	10.43	30.5
18	0	5.78	12.65	0.73	1.52	0.09	9.72	1.8
18	8.7	23.18	8.11	1.88	0.98	0.23	9.59	11.7
18	9	94.78	2.41	2.29	0.25	0.24	11.11	26
20	0	7.45	13.61	1.01	1.59	0.12	9.95	2.9
20	11	6.84	7.69	0.52	0.92	0.06	9.69	23.7
20	13	31.03	3.40	1.05	0.36	0.11	10.95	27.8
21	0	4.49	13.52	0.61	1.83	0.08	8.62	7.2
21	10	10.89	3.85	0.42	0.45	0.05	9.97	21.3
21	13	28.62	3.17	0.91	0.35	0.10	10.49	30
25	0	2.55	23.99	0.61	3.08	0.08	9.08	9.2
25	8	1.65	24.35	0.40	4.80	0.08	5.91	14.9
25	15	0.55	–	–	–	–	–	29.3

Table 26-III continued

1	2	3	4	5	6	7	8	9
25	20	10.39	3.12	0.32	0.34	0.04	10.47	32.4
37	0	2.38	24.00	0.57	3.22	0.08	8.67	9.9
37	8.5	2.03	21.01	0.43	2.90	0.06	8.45	18.4
37	26	4.02	4.82	0.19	0.59	0.02	9.48	32.6

Table 26-IV. Concentrations of total suspended matter (TSM), POC, N_{tot}, C/N in the Yenisey Bay – BP-2000 (Haike et al., raw data).

Station	Sampling depth, m	TSM, mg/l	POC, %	POC, mg/l	N_{tot} %	N mg/l	C/N	S, ‰
13	0	2.31	7.34	0.17	0.79	0.02	9.91	21.6
15	0	4.36	6.62	0.29	0.99	0.04	8.45	6.7
16	0	5.35	5.90	0.32	0.83	0.04	9.33	2.3
17	0	4.22	8.09	0.34	1.25	0.05	7.93	0
19	0	3.46	7.97	0.28	1.22	0.04	8.16	0
20	0	4.02	8.03	0.32	1.23	0.05	7.46	0
21	0	9.43	5.47	0.52	0.78	0.07	8.66	0.3
22	0	5.37	5.22	0.28	0.72	0.04	8.16	6.6
23	0	1.26	9.27	0.12	1.37	0.02	7.00	28.2
24	0	1.8	10.87	0.20	1.62	0.03	7.77	23.8
26	0	0.61	19.00	0.12	2.94	0.02	7.00	18.4
27	0	0.61	18.80	0.11	2.86	0.02	6.41	23.2
13	3.5	3.24	5.33	0.17	0.56	0.02	9.91	25
15	6.5	3.25	6.99	0.23	1.07	0.03	8.94	7.3
16	15.5	8.74	4.56	0.40	0.54	0.05	9.33	12.7
17	18	4.15	7.49	0.31	1.14	0.05	7.23	0.6
21	12	5.29	7.25	0.38	0.92	0.05	8.86	5.9
22	3.7	6.12	4.42	0.27	0.56	0.03	10.49	19.6
23	9.2	1.50	7.21	0.11	0.98	0.01	12.83	30.3
24	16	1.17	11.87	0.14	1.36	0.02	8.16	27.4
26	17	0.37	31.09	0.12	4.71	0.02	7.00	25.6
27	12.5	0.43	18.26	0.08	2.31	0.01	9.32	26.4
13	10.1	19.88	2.73	0.54	0.27	0.05	9.85	29.5
16	24	17.96	3.07	0.55	0.34	0.06	10.69	20.9
22	10.7	9.38	3.00	0.28	0.32	0.03	10.88	29.6
23	32	6.96	2.80	0.20	0.31	0.02	11.66	32.9
24	32	2.19	6.40	0.14	0.58	0.01	16.33	32.3
26	63	2.41	4.04	0.10	0.58	0.01	11.66	33.7
27	74	1.27	3.57	0.05	0.50	0.01	5.83	33.6

Table 26-V. Concentrations of total suspended matter (TSM), POC, N_{tot}, C/N, in the Ob and Yenisey Estuaries – BP-2001 (Haike et al., raw data).

Station	Sampling depth, m	TSM, mg/l	POC, %	POC, mg/l	N_{tot} %	N mg/l	C/N	S, ‰
				Yenisey				
1	0	3.21	8.54	0.27	0.34	0.01	29.24	26.6
3	0	2.89	11.75	0.34	1.34	0.04	10.25	4.4
4	0	2.97	14.75	0.44	1.91	0.06	8.99	0
5	0	3.33	13.29	0.44	1.63	0.05	9.49	0
6	0	2.71	13.48	0.36	1.88	0.05	8.35	0
8	0	1.61	21.85	0.35	3.07	0.05	8.28	0
11	0	2.92	9.17	0.27	1.52	0.04	7.04	0
11	7	2.30	13.69	0.31	2.23	0.05	7.15	1
14	0	5.17	8.02	0.41	1.27	0.06	7.34	0
16	0	3.69	8.97	0.33	1.51	0.05	6.91	0
19	0	3.91	6.44	0.25	0.93	0.04	8.03	6
23	0	3.04	8.40	0.25	1.24	0.04	7.90	4.8
29	0	3.53	6.31	0.22	1.04	0.04	7.10	12.3
4	5	4.10	8.75	0.36	1.30	0.05	7.81	0.1
8	28	3.54	11.00	0.39	1.69	0.06	7.58	0
14	15	4.85	5.06	0.24	0.87	0.04	6.77	0.2
16	22	3.02	10.34	0.31	1.82	0.05	6.63	0
19	5	10.43	4.18	0.44	0.57	0.06	8.51	28
23	7	4.28	5.17	0.22	0.77	0.03	7.79	17.7
11	8	4.34	7.39	0.32	1.28	0.05	6.70	9.6
19	18	52.83	2.38	1.26	0.22	0.12	12.17	32.5
23	15	14.40	3.97	0.57	0.15	0.02	30.79	33
26	28	13.09	1.73	0.23	0.23	0.03	8.80	33.5
				Ob				
68	0	2.91	6.92	0.20	1.02	0.03	7.93	9.8
70	0	11.79	4.79	0.56	0.66	0.08	8.39	0.7
70	6	12.49	2.57	0.32	0.28	0.03	10.66	1.2
72	0	12.96	5.84	0.76	0.71	0.09	9.58	0
73	0	11.85	6.36	0.75	0.87	0.10	8.48	0
79	0	18.85	5.43	1.02	0.72	0.14	8.75	0
68	6	2.90	2.48	0.07	0.29	0.008	10.05	20.5
68	15	3.26	0.78	0.02	0.12	0.004	7.47	31.2
70	12	22.56	1.75	0.39	0.19	0.04	10.41	31.1
82	15	8.21	1.70	0.14	0.22	0.02	8.82	32.3

Table 26-VI. Nutrient concentrations (µM) in the Ob and Yenisey Estuaries – BP-2001 (Tokarev et al., 2003).

Station	Sampling depth, m	P-PO_4	N-NO_3	Si-SiO_3	S, ‰
Yenisey					
01-4	0	0.91	0.26	121.39	0
01-5	0	0.86	1.12	116.52	0
01-6	0	0.60	0.12	78.40	0
01-8	0	1.44	0.20	66.45	0
-“-	27	1.44	0.18	63.70	0
01-9	0	1.34	0.14	124.33	0
01-16	0	0.65	0.12	93.09	0
-“-	27.3	0.49	0.06	95.30	0
01-14	0	1.55	0.16	76.56	0
-“-	18	1.65	0.16	94.20	0.2
01-11	0	1.55	0.24	124.33	0
-“-	7	1.76	0.76	99.34	1
-“-	8.3	–	0.60	80.23	9.6
01-19	0	0.70	–	43.49	6
-“-	5	0.70	–	20.71	28
-“-	23	1.34	–	26.59	32.5
01-23	0	1.34	0.34	77.00	4.8
-“-	8	1.55	0.76	25.26	17.7
-“-	18	1.55	0.64	32.32	22.0
01-26	0	0.70	-	25.58	12.3
-“-	29	1.60	-	27.87	33.0
01-1	0	0.18	1.12	4.45	26.6
Ob					
01-72	0	1.65	0.16	18.23	0
01-73	0	1.34	0.22	64.62	0
01-79	0	1.97	0.40	68.29	0
01-70	0	0.65	0.08	33.38	0.7
-“-	7	0.86	0.12	50.84	1.2
-“-	15	0.60	0.20	54.51	31.1
01-68	0	0.02	0.18	64.62	9.8
-“-	6	0.02	0.18	38.90	20.5
-“-	20	0.39	0.32	17.31	31.2

Table 26-VII. Phosphate concentrations (µM) in the Yenisey Bay-BP-2003 (Vlasova, 2004).

Station	Sampling depth, m	P-PO_4	T,°C	S, ‰
03	0	0.16	6.7	4.9
	7	1.29	0.9	18.5
	14	0.64	–1.3	29.1
04	0	0.16	5.7	3.7
	7.5	0.97	0.9	13.0
	30	1.13	–1.4	30.9
05	0	0.00	1	9.7
	5	0.00	–0.4	15.6
	30	0.81	–1.6	32.3
06	0	0.48	8.2	7.5
	8	0.32	2.6	20.8
	20	0.97	–1.4	29.7
07	0	0.32	7.8	8.7
	6	0.48	4.4	21.1
	94	0.82	–1.0	33.6
08	0	0.97	0.9	9.8
	4	0.16	–1.0	27.4
	44	0.81	–1.5	32.5
09	0	0.56	4.2	20.3
	5	0.16	0.5	25.4
	140	0.81	–1.4	34.2
11	0	0.00	5.8	10.6
	6.5	0.08	0.1	22.0
	29	0.32	-1.6	30.7
13	0	0.73	9.5	2.2
	11	0.97	–0.2	24.1
	26	1.29	–1.3	32.2
14	0	0.16	11.8	1.2
	9	0.97	1.0	24.1
	13	1.29	–1.1	27.7
15	0	0.32	12.8	0.6
	6.5	0.32	10.4	3.3
	10	0.81	3.1	10.9
16	0	1.78	13.9	0
	6	0.73	13.9	0
17	0	0.81	13.3	0
	8	0.81	13.2	0

Table 27 Fluxes of dissolved and particulate trace elements in the Ob, Yenisey and Lena Rivers (Cd, Hg-t/y, another elements – 10^3 t/y).

River		Cu	Zn	Ni	Pb	Cd	Cr	Mn	Sr	Ba	V	Zr	As	Hg
Ob	diss.	1.09	–	0.78		1.2	0.14	9						0.2
	part.	0.71	4.07	0.81	0.53	8.0	1.67	34	2.24	6.6	2.1	1.8	0.56	0.8
	?	1.80	–	1.59		9.2	1.81	43						1
	F, %	60.5	–	49.0		13.0	7.7	20.7						20
Yenisey	diss.	0.99	0.81	0.31	0.0034	0.9	–	–	–	–	–	–	–	0.2
	part.	0.47	1.03	0.36	014.	90	0.61	12.9	12.9	2.0	0.72.	0.61	0.04	0.3
	?	1.46	1.84	0.67	0.143	91	–	–	–	–	–	–	–	0.5
	F, %	59.3	44.0	46.3	2.4	1.0	–	–	–	–	–	–	–	40
Lena	diss.	0.42	0.22	0.16	0.018	3	–	–	–	–	–	–	–	0.4
	part.	0.70	3.1	0.99	0.56	13	–	33	4.0	14.9	2.0	2.73	0.19	4
	?	1.12	3.32	1.15	0.578	16	–	–	–	–	–	–	–	4.4
	F, %	37.5	6.6	13.9	3.1	18.7	–	–	–	–	–	–	–	9.1
Total Eurazian Arctic	diss.	4.8	2.2	3.8	0.035	10	–	–	–	–	–	–	-	1.5
	part.	5.1	21.6	5.4	2.96	70	–	225	17.9	58	12.7	17.6	2.0	9.6
	?	9.9	23.8	9.2	3.0	80	–	–	–	–	–	–	–	11
	F, %	48.5	9.2	41.3	1.2	12.5	–	–	–	–	–	–	–	13.6

Table 28 Enrichment factor of elements in SPM of the Ob and Yenisey Estuaries (DM-1993).

Group of elements	Enrichment factor		Comments
	Ob Estuary	Yenisey Estuary	
Group 1 Fe, Hf, Th, Zr, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu	<2	<2	These elements remain unaltered when compared to their av. content in river SPM
Group 2			These elements accumulate in SPM at salinity 15-20‰ (frontal zone 2)
Cr	4-9	5-8	
Ba	3-8	4-9	
Cs	2-2.7	3-7.5	
Co	3-5	4-9	
Group 3 Br	36	13-150	Increasing is visible at salinity 5-10 ‰ (frontal zone 1) and especially at salinity 15-20 ‰ (frontal zone 2)

* Enrichment factor - $(Me/Sc)_{\text{estuary SPM}}/(Me/Sc)_{\text{av. river SPM}}$

Table 29 Enrichment factor of elements in SPM of the Yenisey Estuary (BP-2000).

Group of elements	Enrichment factor	Comments
Group 1 U	1	Unaltered when compared to its av. content in river SPM in full range of salinity
Group 2 V, Zn, Ni, Y	1-1.5	Unaltered when compared to their av. content in river SPM and increased at S ≈ 20-30 ‰
Group 3 Mn, Cd, As, Ba, Cu, Pb, Co	1.5-3.5	As Group 2 but higher enrichment factor of salinity ≈ 20-30 ‰

* EF = (Me/Al) estuary SPM/(Me/Al) river SPM.

Table 30 Enrichment factor of elements in SPM of the Ob and Yenisy Estuaries (BP-2001).

Group of elements	Enrichment factor		Comments
	Ob Estuary	Yenisey Estuary	
Group 1 V, Zn, Co	1	1	Unaltered when compared to their av. content in river SPM
Group 2			
Ba	<1	4	These elements in the Yenisey Estuary demonstrate at salinity 12-17 ‰ and max at 26-30 ‰
As	1	2-6	
Sr	1	4-6	
Ni	1	6-7	
Group 3			
Cr	1	9-16	The same pattern as in Group 2 but higher enrichments in both ranges of salinity
Cu	1	11-26	
Cd	0.7-1.5	6-13	
Zn	1	10-13	
Pb	0.7-1.6	16-18	

* EF= $(Me/Al)_{\text{estuary SPM}}/(Me/Al)_{\text{av. river SPM}}$

Table 31 Net fluxes of major elements in dissolved and particulate forms in the Ob and Yenisey Estuaries (10^3t/y). F,%= $Q_{diss}/\ Q_{diss}+Q_{part}$

Estuary		Ca	Mg	K	Fe	Ti	P
Ob	diss.	7676	2060	1535	58.5	–	–
	susp.	16	12	16	99.2	5.7	3.3-7.0
	∑	7692	2072	1551	157.7	–	–
	K, %	99.8	99.4	99.0	37.1	–	–
Yenisey	diss.	9850	2050	620	59.5	–	–
	susp.	9	8	6	29.7	1.8	0.9-2.7
	∑	9859	2058	626	89.2	–	–
	K, %	99.9	99.6	99.0	66.7	–	–
Lena	diss.	8450	2310	890	16.8	–	–
	susp.	37	38	60	103	10.2	7.8
	∑	8487	2348	950	119.8	–	–
	K, %	99.6	98.4	93.7	14.0	–	–
Total Eurasian Arctic	diss.	45980	10770	42.50	257.5	–	–
	susp.	138	126	146	536.5	36.7	–
	∑	46118	10896	4396	794	–	–
	K, %	99.7	98.8	96.7	32.4	–	–

Table 32 Net fluxes of dissolved and particulate trace elements in the Ob, Yenisey and Lena mixing zones and in the total Eurasian Arctic (10^3 t/y).

River basin		Fe	Cu	Ni	Pb	Zn	Cd	Cr	Mn	Sr	Ba	V	Zr	As
Ob	diss.	12.7	0.84	0.71	0.002	–	–	–	–	–	–	–	–	–
	susp.	99.2	0.057	0.065	0.042	0.32	0.0006	0.13	2.7	0.18	0.53	0.17	0.14	0.045
	?	111.9	0.90	0.77	0.044	–	–	–	–	–	–	–	–	–
	K. %	11.3	93.3	91.6	4.5	–	–	–	–	–	–	–	–	–
Yenisey	diss.	11.5	1.1	0.54	0.0025	–	–	–	–	–	–	–	–	–
	susp.	29.7	0.063	0.049	0.019	0.14	0.012	0.082	1.7	0.14	0.27	0.097	0.082	0.0054
	?	41.2	1.16	0.59	0.025	–	–	–	–	–	–	–	–	–
	K. %	27.9	94.6	91.5	11.6	–	–	–	–	–	–	–	–	–
Lena	diss.	1.89	0.89	0.37	0.018	0.042	–	–	–	–	–	–	–	–
	susp.	10.34	0.095	0.133	0.076	0.42	0.0017	–	4.45	0.54	2.0	0.27	0.37	0.026
	?	10.53	0.985	0.503	0.094	0.46	–	–	–	–	–	–	–	–
	K. %	1.8	90.3	73.5	19.1	9.1	–	–	–	–	–		–	–
Total Eurasian Arctic	diss.	49.2	5.33	3.09	0.042	–	–	–	–	–	–	–	–	–
	susp.	536.5	0.51	0.54	0.296	2.16	0.007	–	22.5	1.79	5.8	1.27	1.76	0.20
	?	585.7	6.02	3.63	0.338	–	–	–	–	–	–	–	–	–
	K. %	8.4	88.5	85.1	12.4	–	–	–	–	–	–	–	–	–
Net flux Gross flux	?	0.10	0.60	0.39	0.11	–	–	–	–	–	–	–	–	–

Table 33 Granulometric composition of the facies of bottom sediments in the Kara Sea coastal zone (%) (Levitan et al., 2005).

Facie	>10	10-7	7-5	5-3	3-2	2-1	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001
	mm													
A (n=8)	3.52	0.61	0.58	0.12	0.22	0.16	0.51	7.48	14.92	16.10	2.24	8.59	18.42	26.53
B1 (n=13)	0.00	0.00	0.00	0.00	0.19	0.32	1.42	10.71	15.08	11.89	2.42	8.24	17.85	31.88
B2 (n=13)	0.00	0.00	0.00	0.00	0.00	0.40	0.10	0.53	5.70	2.91	4.44	14.72	29.23	41.97
C3 (n=19)	0.00	0.00	0.00	0.00	0.00	0.43	0.13	1.19	19.17	12.47	3.26	10.14	20.76	32.46
C4 (n=12)	0.00	0.00	0.00	0.00	0.00	0.38	0.20	0.26	1.38	2.49	2.35	19.15	31.92	41.87
D1 (n=9)	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.15	1.24	2.28	0.45	14.13	30.69	50.71

Table 34 Light minerals in different facies (%) (Levitan et al., 2005)

Facie	Quartz	Basic and middle plagioclases	Acid plagioclases	Potassium feldspars	Sum of feldspars	Q/Fs
A (n=8)	68.2	3.0	5.3	12.3	20.6	3.3
B1 (n=9)	55.4	6.8	8.4	5.8	21.0	2.6
B2 (n=13)	58.5	3.9	6.5	14.1	24.5	2.4
C3 (n=19)	65.8	2.5	3.9	18.3	24.7	2.7
C4 (n=12)	66.4	3.7	1.4	21.9	27.0	2.5
D1 (n=9)	59.0	0.5	7.1	13.7	21.3	2.8

Table 35 Clay mierals in different facies (%) (Levitan et al., 2005).

Facie	Illite	Smectite	Sm/Il	Chlorite	Kaolinite
A (n=11)	24	46	1.9	16	14
B (n=30)	25	44	1.8	17	14
C3 (n=23)	22	47	2.1	16	15
C4 (n=16)	23	49	2.1	15	13
D1 (n=7)	30	44	1.5	16	10
D2 (n=4))	38	39	1.0	14	9

Table 36 Main heavy minerals (fraction o.1-0.05 mm) in different facies (%) (Levitan et al., 2005).

Facie	Clinopiro-xene	Epidote	Black ore minerals	Horn blende	Garnet	ClP/Ep
A (n=8)	31.6	17.6	24.7	7.7	2.9	1.7
B1 (n=9)	37.2	13.0	25.7	8.2	3.0	3.3
B2 (n=13)	44.4	12.1	14.3	8.9	3.5	3.3
C3 (n=19)	31.0	14.5	21.7	8.3	6.0	2.0
C4 (n=12)	36.2	14.8	18.8	5.8	5.5	2.5
D1 (n=9)	21.9	23.5	19.8	5.1	8.0	0.9
D2 (n=4)	21.7	26.8	17.8	7.0	7.6	0.8

Table 37 Ratios of element contents in fr.>50µm to fr.<4µm in bottom sediments of the Ob and Yenisey Estuaries (Yenisey sediments- ICP, AAS and INAA determinations, Ob sediments- INAA determinations only).

Element	Yenisey sediments		Ob sediments	
	St. 4409 (silt oxid.)	St. 4399 (clay oxid.)	St. 4417 (silt red.)	St. 4397 (clay oxid.)
Si	1.7	1.5	–	–
Ca	4.5	5.5	1.0	0.9
Hf	–	2.6	1.3	1.0
K	0.8	0.9	–	0.95
Na	1.6	1.0	0.85	0.90
TOC	0.21	0.08	–	–
Al	0.52	0.83	–	–
Fe	0.30	0.19	0.06	0.07
Mg	0.47	0.24	–	–
Mn	0.7	0.38	–	–
Cu	0.08	0.10	–	–
Pb	0.11	0.36	–	–
Ni	0.27	0.14	–	–
Zn	0.13	0.14	–	–
Co	0.18	0.23	0.17	0.09
Cr	0.53	0.26	0.09	0.20
Rb	–	0.42	0.26	0.22
Cs	–	0.10	0.01	0.02
Sc	–	0.38	0.11	0.17
Th	–	0.71	0.15	0.59

Table 38 The expeditions to the Kara Sea (1993-2003).

n/n	Cruise	Year	Dates of the cruise	Latitudes of the estuarine transects, °N		Full range of salinity in the cruise
				Ob	Yenisey	
1	49 DM*	1993	14.08-15.10	68°49-75°59	71°02-76°00	0-34
2	28 BP	1997	14.08-28.09	72°10-73°54 72°35-73°10	72°05-73°32 72°05-73°32	1.2-21
3	32 BP	1999	22.08-08.09	72°10-74°30	72°28-74°30 72°20-74°00	0.6-18
4	35 BP	2000	31.08-24.09	–	69°50-76°57	0-34
5	36 BP	2001	11.08-15.09	68°50-73°11	71°49-74°00	0-34.6
6	37 BP	2002	26.09-13.10	68°40-72°40	–	0-26.4
7	38 BP	2003	18.08-26.08	–	71°50-74°59	0.2-29

* DM - R/V "Dmitry Mendeleev"
BP - R/A "Academic Boris Petrov"

Table 39 The main physico-geographical characteristics of the river and delta-estuarine areas.

	Ob	Yenisey
River		
Area, 10^6 km^2	2.54	2.59
Length, km	3650	3844
Water discharge, km^3/y	404	620
Specific discharge, l/sec·km^2	5.0	7.6
SPM discharge, 10^6 t/y	15.5	4.7
Average SPM concentration, mg/l	37	8
Specific SPM discharge, t/km^2	6.1	1.8
Number of reservoirs	13	8
Total volume of reservoirs, km^3	75.2	473.9
$K=\Sigma$reserv./Q	0.18	0.81
Delta-estuarine area		
Delta:		
Length, km	144	196
Area, km^2	3250 (with islands)	4500
Estuary:		
Length, km	760	351
Width, km	35-80	15-30
Depth, m	10-12	18-30
Area, km^2	408000	20000
Total length of the delta-estuarine area, km	860	547
Total area of the delta-estuarine area, km^2 (Ob - Taz + delta)	55000	24500
Water currents, m/sec		
at flood time		0.8-1.2
at low water		0.3-0.5
Type of estuary	Salt-wedge	Salt-wedge

Table 40 The frontal hydrochemical zones in the Ob and Yenisey Estuaries.

Expedition	Estuary	Dates of works in the estuary	Salinity of surface waters, ‰	Frontal zone		
				Latitudes, °N	Grand T, °C/km	Grand S ‰/km
DM-1993	OB	15-29.09	0-24	71°-73°30	0.017	0.055
					(surface waters)	
					0,042	0.16
					(depth >8-10m)	
	Yenisey	16-24.09	0-24.5	to south from 72°30	–	–
				≈74° (with 25km)	1	3.2
BP-1997	Ob	13-15.09	2.4-12.7	72°30-72°50	0.07	0.3
		22-23.09	13.4-20.8	Absent		
	Yenisey	17-18.09	1.2-15.3	Absent		
		19-20.09	1.2-7	Absent		
BP-1999	Ob	24.08-07.09	1.8-9.9	≈73°	0.02	0.07
	Yenisey	24.08-08.09	2.6-7.4	≈74°	–	–
		26.08-06.09	4.7-12.7	≈74°	–	–
BP-2000	Yenisey	05-19.09	0-27	72°40-73°30	0.5	0.2
BP-2001	Ob	07-11.09	0-9.8	72°40-73°10	0.08	0.15
	Yenisey	18-23.08	0-26.6	72°05-72°35	0.2	0.3
BP-2002	Ob	08-09.10	0-8.2	71°45-72°40	0.02	0.08
BP-2003	Yenisey	19-24.08	0.2-8	72°15-72°50	–	–

Table 41 Chlorophyll "a" concentrations (µg/l) in the Ob and Yenisey Estuaries in different years.

Expedition, year	70-72°N fresh	72-74°N fresh/brackish	74-76°N brackish/marine	76-78°N marine	Reference
1993 Ob	2.7-21.7	1.6-2.05	0.66-0.86	–	Vedernikov et al., 1994
Yenisey	4.5-5.5	1.8-3.3	0.33-0.42	–	– " –
1997 Ob	–	0-2	–	–	Nothig et al., 2003
Yenisey	–	1- >3	–	–	– " –
1999 Ob	–	3- >5	>5	–	Nothig et al., 2003
Yenisey	–	1- (3-5)	>5	–	– " –
2000 Ob	–	0-2	0-1	0-1	Nothig et al., 2003
Yenisey	1- >3	0-2	0-2	0-1	– " –
2001 Ob and Yenisey	–	≈ 1 (73-75°N)		0.13-1	Beude and Nothig, 2002

(* Data by Nothig et al., 2003 were read from the figures of Chl.a distribution, the table's data were not presented.

Table 42 Integral picture of the intensity of biogeochemical processes in two estuaries.

Year	Estuary	River run-off	Hydrological fronts (grad T, grad S)	Grad SPM	River end member					Bioactivity (chl.a, PP)	Intensity of trace element involvment into biocycle (EF)	Comments (integral intensity of biogeochemical processes)
					DOC,	POC,	NO_3	PO_4	Si			
					µM	%	µM					
1993	Ob Yenisey		wide, weak two fronts, one sharp	S to N S to N	700 350	7-10 8-13	2.5 0.1	1.4 0.1	50 90	moderate higher	moderate moderate	Yen>Ob
1997	Ob* Yenisey *	typical typical	moderate no front	S to N S to N	650 550	8-9 3-6	1.1 0.14	0.50 0.34	25 80	moderate moderate	moderate moderate	Yen?Ob
1999	Ob* Yenisey *	higher higher	very weak very weak	S to N S to N	600 740	– –	0.1-0.4 <0.02-0.08	1.6 1.4	8-10 10-15	highest higher	– –	Ob>Yen (?)
2000	Ob Yenisey	typical typical	– moderate	– S to N	600 680	– 5-8	– 0.06-3.1	– 0.6	– 60-128	low low	– low	?
2001	Ob Yenisey		weak moderate	S to N no grad	– –	5-7 8-15	0.2-0.4 0.006-0.24	1.6-2.1 0.6-1.6	70-100 70-130	low low	low moderate	Yen>Ob

* River end member was practically absent. The transects were started from salinity ca. 2-4 ‰

Table 43 Mean values of selected element to Al and to K ratios in SPM and bottom sediments of the Ob and Yenisey Estuaries. For comparison, the same ratios are given for the Siberian trap basalts and average shales (Lightfoot et al., 1990; Taylor and McLennan, 1985).

	Mg/K	Si/Al	Mg/Al	K/Al	Ca/Al	Fe/Al	Ti/Al	Ni*/Al	Cr*/Al	Sr*/Al	Rb*/Al	V*/Al	Ce*/Al	Zr*/Al
Siberian trap basalts	16	2.62	0.48	0.03	0.92	1	0.08	11.5	20	24	0.5	30		11
Average shales	0.42	2.93	0.17	0.30	0.09	0.5	0.06	5.5	11	20	16	15	7.4	21
SPM (this work)														
Ob	0.69	4.22	0.16	0.23	0.21	1.35	0.08	8.8	18.3	24.5	–	22.7		20
Yenisey	1.41	4.83	0.27	0.19	0.30	1.0	0.06	15.9	27.6	32.9	–	29.8		27.7
SPM (Gordeev et al., 1995)														
Ob	0.75	3.56	0.17	0.23	0.12	0.87	–	5.5	14.4	–	–	–	–	–
Yenisey	1.41	3.49	0.29	0.20	0.27	0.90	–	11.8	19.9	–	–	–	–	–
SPM (Lukashin et al., 1999)														
Ob	–	4.24	–	–	0.043	2.16	0.04	28	14.3	26	–	30.8	–	–
Yenisey	–	3.58	–	–	0.12	1.29	0.06	22	20	39	–	27.8	–	–
Bottom sediments (Gordeev et al., 1995)														
Ob	0.61	4.50	0.17	0.29	0.12	0.80	–	7.4	12.8	–	–	–	–	–
Yenisey	1.28	4.78	0.28	0.22	0.35	0.74	–	8.7	16	–	–	–	–	–
Bottom sediments (Schoster and Stein, 1999)														
Ob	0.71	4.42	0.18	0.28	0.12	0.83	0.07	5.9	14	25	13	21	–	32
Yenisey	1.40	3.53	0.27	0.18	0.28	0.79	0.08	7.6	15	32	10	23	–	22

* - n×10^{-4}

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