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The turbidity maximum zone of the Yenisei River (Siberia) and its impact on organic and inorganic proxies

A.C. Gebhardt [a,*], F. Schoster [a], B. Gaye-Haake [b], B. Beeskow [c], V. Rachold [d], D. Unger [e], V. Ittekkot [e]

[a] Alfred Wegener Institute for Polar and Marine Research, Columbusstraße, 27515 Bremerhaven, Germany
[b] Institute for Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstraße 55, 20146 Hamburg, Germany
[c] School of Earth Science and Geography, Kingston University, Penrhyn Road, Kingston Upon Thames, Surrey, KT1 2EE, United Kingdom
[d] Alfred Wegener Institute for Polar and Marine Research, Telegrafenberg A43, 14473 Potsdam, Germany
[e] Centre for Marine Tropical Ecology, Fahrenheitstraße 6, 28359 Bremen, Germany

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Abstract

A general overview of the processes taking place in the summer mixing zone of the fresh Yenisei River water with the marine waters of the Kara Sea is given in this study, with special emphasis on the interaction between bulk (total suspended matter), inorganic (Fe, Mn) and organic (suspended organic carbon, suspended nitrogen) proxies. Within the mixing zone, a zone of enhanced turbidity (maximum turbidity zone) was observed comparable to studies in other rivers. Flocculation of particles due to changes in salinity and hydrography cause this maximum turbidity zone, and resuspension additionally enhances the turbidity in the near-bottom layers. Organic matter behaves conservatively in the mixing zone in terms of its percentage of suspended matter. It, however, undergoes degradation as revealed by amino acid data. Inorganic, redox- and salinity-sensitive, proxies (Mn, Fe) behave non-conservatively. Dissolved iron is removed at low salinities (<2) due to precipitation of iron oxyhydroxides and adsorption of manganese on suspended particles, enhancing the Mn/Al ratio of the suspended matter in the same zone. At higher salinities within the mixing zone, Fe/Al and Mn/Al ratios of the suspended particles are depleted due to resuspension of sediment with lower Fe/Al and Mn/Al ratios. Dissolved manganese concentrations are significantly higher in the near-bottom layers of the mixing zone due to release from the anoxic sediment. All things considered, the Yenisei River mixing zone shows patterns similar to other world's rivers.

Keywords: mixing zone; turbidity maximum; carbon cycle; Arctic Ocean; Kara Sea

1. Introduction

Estuaries occupy less than 10% of the ocean's surface (Lisitsyn, 1995), but play an important role in the global cycle of divers substances (e.g. organic matter, nutrients, metals). Estuaries and coastal areas trap significant quantities of suspended and dissolved matter and, thus, act as filter between the terrestrial and the marine realm. Mixing of riverine freshwater and marine saline water and the associated changes in physicochemical properties lead to physical, chemical and biochemical processes affecting the dissolved and suspended load of the river. During the late 1970s, a broad interest in the processes taking place in the mixing zone arouse (e.g. Cronin, 1975; Wiley, 1976, 1978; Kennedy, 1980, 1982, 1984). Despite the large number of studies, some of the processes in estuaries are still not well understood. Some parts of the river load seem not to be affected by

* Corresponding author.
E-mail address: cgebhardt@awi-bremerhaven.de (A.C. Gebhardt).

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the estuarine processes, whereas others are trapped or mobilized in the mixing zone. This ability of estuaries to remove or retain material in solution and suspension makes estuaries important in terms of environmental questions.

During the last decades, studies about the removal and mobilization processes were carried out in several estuaries (e.g. Lena River, Gordeev and Shevchenko, 1995; Cauwet and Sidorov, 1996; St. Lawrence River, Bewers and Yeats, 1978, 1979; Cossa and Poulet, 1978; Gobeil et al., 1981; Hamblin, 1989; Lucotte, 1989; Changjiang River, Milliman et al., 1985; Cauwet and Mackenzie, 1993; Jiufa and Chen, 1998). A zone of maximum turbidity is generally observed in estuaries at the convergence of the downstream flowing surface water and the upstream flowing salt wedge of marine water (Bowden, 1984). This zone is characterized by high concentrations of suspended matter, higher than upstream in the river or downstream in the estuary. The estuarine circulation pattern has an effect on the location and strength of the turbidity maximum zone. This site of high suspended matter concentrations provides an ideal site for physical, chemical and biological reactions between dissolved and particulate species as well as interactions among particulate species, so that much of the riverine material is deposited.

Lisitsyn (1995) calculated that in what he calls the "marginal filter", about 93–95% of the suspended and about 20–40% of the dissolved riverine material is deposited worldwide. He slightly modified his statement for the Polar Regions where rivers drain areas of permafrost and are more influenced by seasonal variations, e.g. by ice cover and snow during winter. Lisitsyn (1995) distinguishes between two different marginal filter regimes in the Ob and Yenisei rivers: (a) a short summer regime with the main part of water and solid material delivered to the Kara Sea; and (b) a rather long winter regime with low water and suspension discharges. He further introduces a so-called ice marginal filter: during ice production, the saline water forms dense plumes sinking in the water column and transporting some of the marginal filter sediment away from its initial position.

In this study, we intend to characterize the processes taking place in the Yenisei River estuary and compare these findings with the adjacent Ob River estuary as well as with rivers from other non-polar regions. However, as all our data originate from the short Arctic summer period, we are only able to evaluate the summer situation.

2. Study area

The Kara Sea is one of the Arctic shelf seas of Northern Siberia (Fig. 1). The central and the eastern parts of the Kara Sea are dominated by the Ob and Yenisei estuaries (=Yamal Plateau) with a characteristic depth of 25–30 m. More than one third of the total freshwater discharge to the Arctic Ocean is into the Kara Sea, mainly via Ob and Yenisei rivers (Aagaard and Carmack, 1989).

The Yenisei River draining into the Kara Sea is Siberia's largest river with a drainage area of 2.58×10^6 km^2 and a length of 3844 km (Milliman and Meade, 1983; Milliman, 1991; Telang et al., 1991; Gordeev, 2000). The Yenisei bed crosses igneous basement rocks and fills two large reservoirs in its upper reaches, and flows through the West Siberian Plain in regions of permafrost in its lower reaches. Along the banks, the taiga is gradually replaced by forest tundra. The freshwater discharge to the Kara Sea is highly seasonal with the main discharge occurring during spring and summer, part of which occurs while the Southern Kara Sea is ice-covered. The Kara Sea is almost entirely ice-covered from October to May (e.g. Pavlov and Pfirman, 1995) with only a small narrow polynya north of the fast-ice zone remaining ice-free due to prevailing offshore winds (Pavlov and Pfirman, 1995; Harms et al., 2000). During the summer months, deep water supplied from the central Arctic Ocean forms a stable salt wedge having salinities >30 in the Yenisei River.

Large amounts of river suspension have built up thick packages of sediments mostly in the outer estuary and the southernmost Kara Sea (Dittmers et al., 2003; Stein and Fahl, 2004). It has been assumed that the major amount of organic carbon deposited in the Kara Sea is of riverine origin (Stein and Fahl, 2004, and references therein).

3. Data used for this study

In order to get detailed information on the processes taking place in the mixing zone of river and sea water, we combine different data from the Yenisei River estuary. Most of the data were obtained within the framework of the German-Russian SIRRO project (Siberian River Run-Off) on three *RV Akademik Boris Petrov* cruises between 1997 and 2000 (Matthiessen and Stepanets, 1998; Matthiessen et al., 1999; Stein and Stepanets, 2000, 2001). Additionally, sediment surface samples from the international *RV Dmitriy Mendeleev* expedition in 1993 (Lisitsyn and Vinogradov, 1995) were used in this study. All suspended and dissolved matter samples are from the *Akademik Boris Petrov* 2000 cruise in order to avoid effects due to different conditions in different years. Nevertheless, surface sediment samples originate from different years as they are not affected by interannual variations.

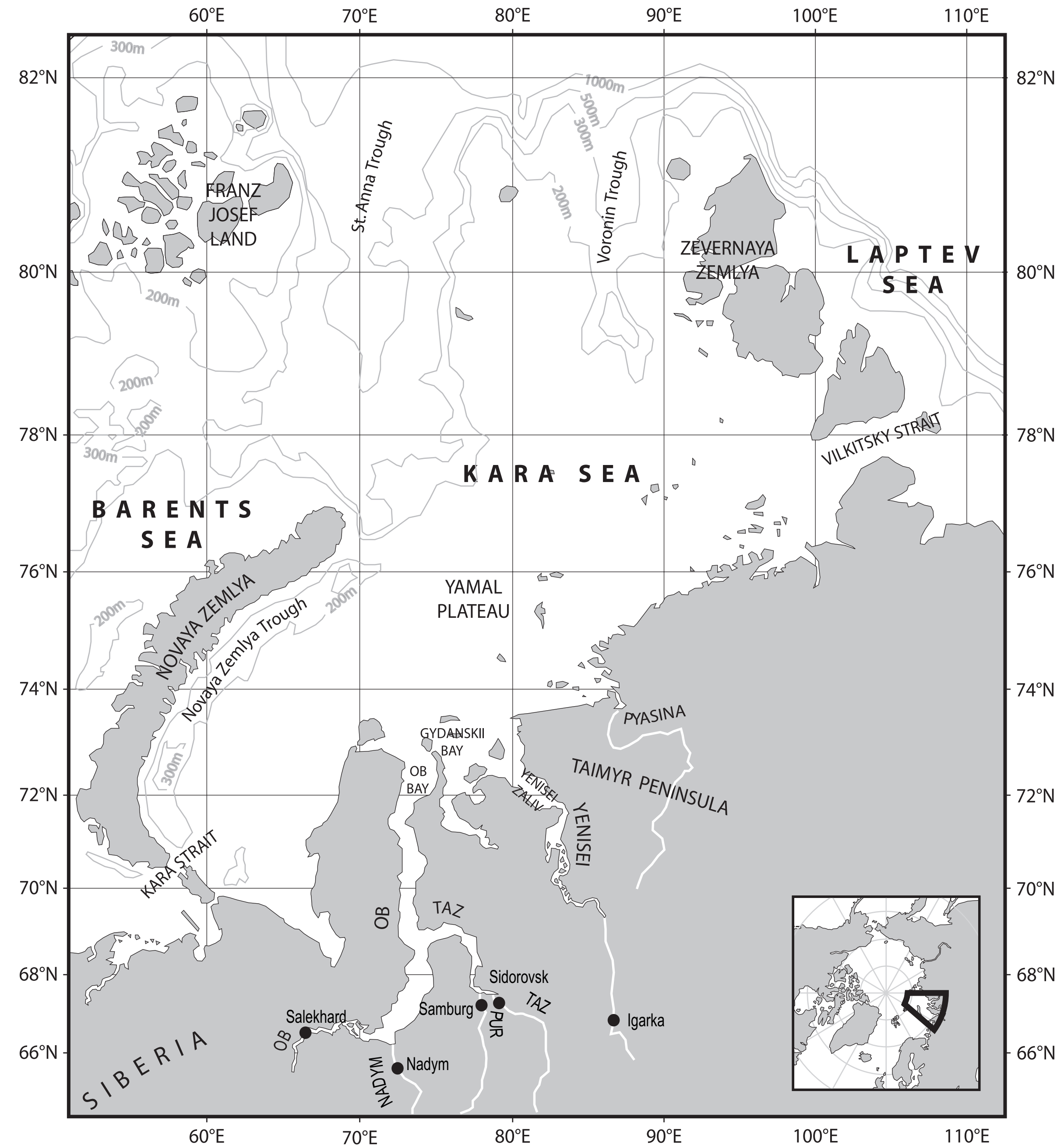

Fig. 1. General overview of the study area (after Gebhardt et al., 2004).

TSM fluxes were calculated from glass fiber filter (Gebhardt et al., 2004). Total particulate carbon and nitrogen were measured using a Carlo Erba Nitrogen Analyzer 1500. The precision of this method is 0.05% for carbon and 0.005% for nitrogen. Carbonate percentages of suspended matter samples were initially determined using a Wösthoff Charmograph 6. The typical standard deviation of results is 1%. All measurements were below 0.2% of carbonate with most below 0.1%. Because this is close to the error range of total carbon measurements, we have further assumed that total carbon of all samples equals total organic carbon (Gebhardt et al., 2004).

Details of amino acid analyses, calculation of the Reactivity Index (RI) as well as total organic carbon of surface sediment (TOC) can be found in Unger et al. (2005). Analytical procedure for preparation of suspended Mn/Al and Fe/Al as well as dissolved Mn and Fe are given in Beeskow and Rachold (2003), surface sediment Mn/Al and Fe/Al data originate from Schoster et al. (2000). Salinity is always given as a ratio (Practical Salinity Unit).

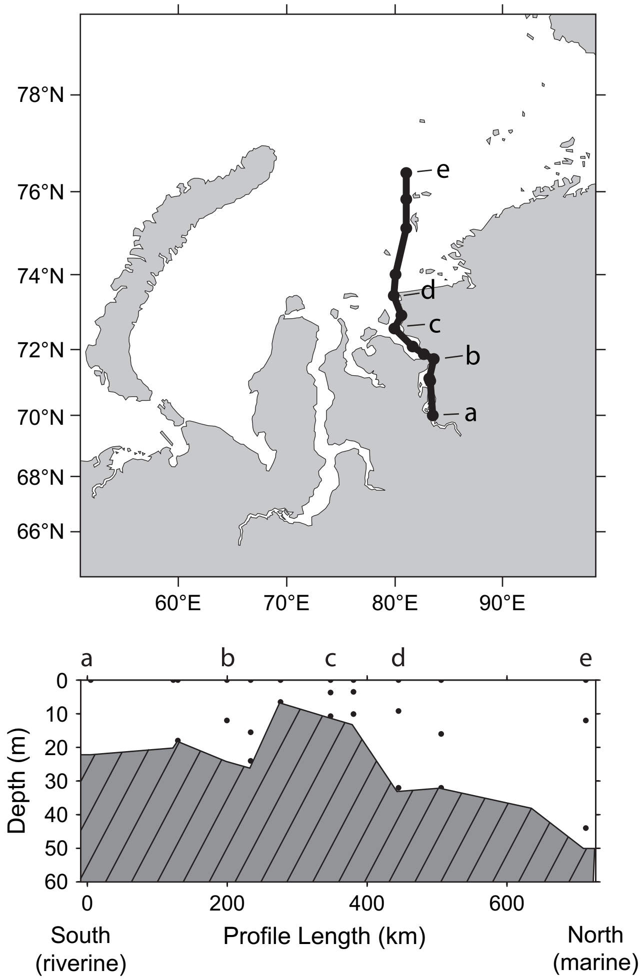

Fig. 2. Yenisei River profile used in this study. Dots mark sampling points.

For investigation of the processes active in the estuary and, in particular, in the mixing zone between riverine freshwater and marine saline water, we chose a transect from 70 °N in the southern part of the Yenisei River (salinity = 0) to 76.4 °N in the central Kara Sea (salinity = 29.1) (Fig. 2).

4. The marginal filter of the Yenisei River

4.1. Salinity and TSM

The Kara Sea surface waters are underlain by highly saline deep waters with a pycnocline separating the two water masses (as reported in Burenkov and Vasil'kov, 1995) (Fig. 3a). River run-off forms a plume of low saline water north of the two river estuaries (Fig. 4a). Water with salinities of 20–30 enters the estuary as salt intrusions, forming a stable salt wedge in the Yenisei River which penetrates as far south as a narrows at 71.6 °N, as revealed by a salt intrusion lens south of the narrows (Fig. 3a). A lens of highly saline surface water (about 25) was observed just north of the Yenisei estuary (Fig. 4a).

Zones of TSM concentration maxima (TSM concentrations > 10 mg/l) are found in two areas at the river bottom (Fig. 5); (a) where the narrows at 71.6 °N widens towards north; and (b) at the Yenisei River–Kara Sea interface. Both areas are characterized by hydrographic changes: (a) flow speed is high at the narrows functioning as a funnel for the Yenisei water. Where the narrow widens, the flow speed changes and vortices cause resuspension of bottom material. (b) At the opening of the river to the Kara Sea, marine deep water intrudes into the river mouth. This water mass of marine origin and initially marine composition causes turbulences at its interface to the river bottom, resulting in resuspension of sediment. Furthermore, at the interface between the overlying riverine water and the deep marine water where the pycnocline develops, the shear stress is enhanced due to the diametrical current directions.

Enhanced TSM concentrations at the river bottom can be explained by resuspension. Enhanced values within the surface water must be explained by a different process. Kranck (1984) points out that large flocs with higher settling velocities sink to the river bottom where they are destructed due to different settings and resuspended as smaller particles, forming part of the turbidity maximum. Distinct increases in surface TSM concentration from values < 5 mg/l to values between 5 and 8 mg/l are observed in the mixing zone of riverine freshwater and marine water at salinities between 0.1 and 10. Electrochemically induced precipitation and flocculation of colloidal as well as dissolved material play important roles in the removal of substances such as iron and manganese as well as fine suspended matter (Kranck, 1984). It is still not clear whether the salinity change or the change in hydrography is the main reason for aggregation and disaggregation of particles (e.g. Burban et al., 1989, 1990; Lick et al., 1993; Serra et al., 1997; Thill et al., 2001; Winterwerp, 2002). As changes in hydrography and salinity occur at the same locations in the Yenisei River, it is not clearly distinguishable which process is eventually responsible for the flocculation of suspended matter in this river.

4.2. Organic proxies

To study the effect of estuarine processes on organic matter, particulate and total organic carbon (POC and TOC) as well as particulate and total nitrogen (PN and TN, comprising organic and inorganic nitrogen) were studied. Percentages rather than absolute concentrations were used to avoid concentration-dependent phenomena. Amino acid data (in particular the RI index) was used to determine the degradational state of the organic matter.

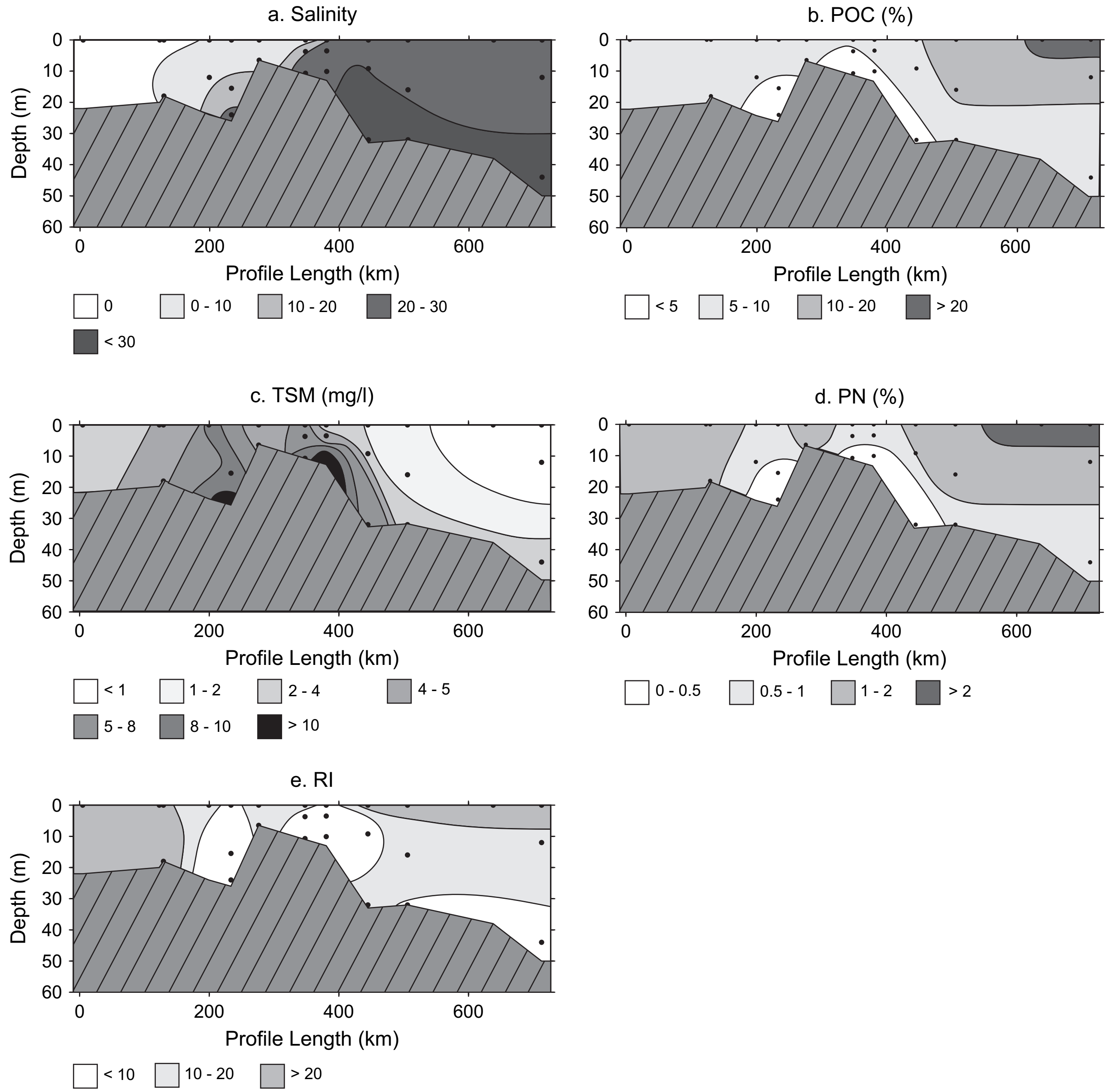

Fig. 3. Salinity, TSM and organic proxies profiles. (a) Salinity, (b) POC (%), (c) TSM (mg/l), (d) PN (%), (e) RI. Dots mark sampling points.

POC percentages are relatively constant between 5 and 10% from the southernmost point of the river to the river mouth (Fig. 3b). Nevertheless, POC values are lower in the areas of resuspension indicated by enhanced TSM concentrations. Sediment has much lower TOC concentrations of about 2–2.5% (Fig. 4b), and if sediment of lower TOC is resuspended, it dilutes the POC content of the original suspended matter; this phenomenon in turn confirms the process of resuspension in these areas. PN behaves relatively similar to POC, with zones of decreased PN percentages due to resuspension of sediment with lower TN content (Figs. 3d and 4c). Both POC and PN concentrations remain constant in the surface mixing zone. This confirms that (a) resuspension barely affects the surface layers of the Yenisei River; and (b) flocculation of dissolved organic matter is of minor importance, as already reported by Köhler et al. (2003). Enhanced POC and PN concentrations are measured in surface waters about 600 km north of the estuary. Low TSM values in the same area allow deeper light penetration, which in turn enables higher primary productivity.

Details of amino acid analyses of suspended matter and surface sediments from the Kara Sea have been presented by Unger et al. (2005). They have shown that, among the biogeochemical indicators derived from

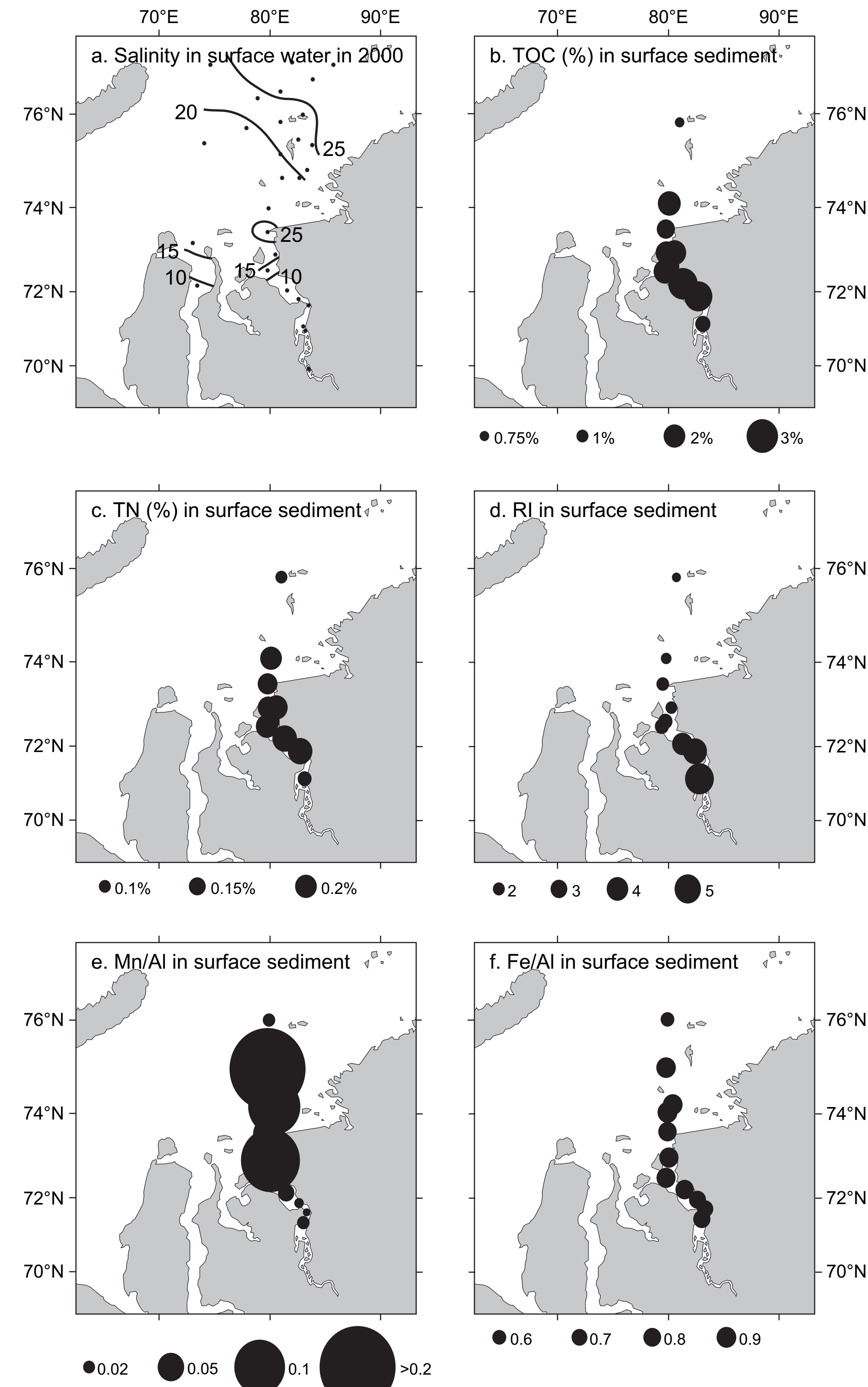

Fig. 4. Salinity and surface sediment geochemistry maps. (a) Salinity of surface water, (b) TOC (%) of surface sediment, (c) TN (%) of surface sediment, (d) RI of surface sediment, (e) Mn/Al of surface sediment, (f) Fe/Al of surface sediment. Dots mark sampling points.

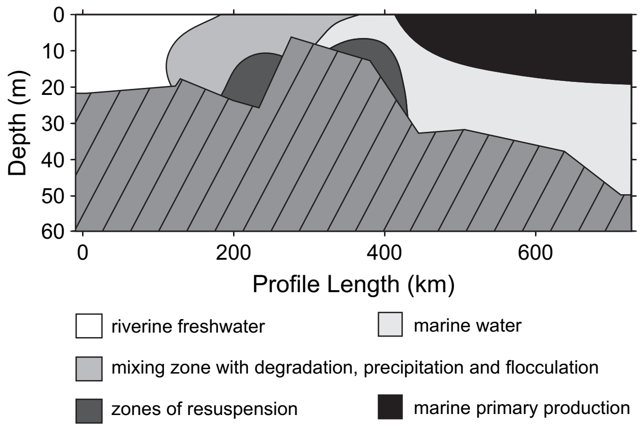

Fig. 5. Simplified model of the Yenisei River profile.

amino acid contents and molar percentages, the Reactivity Index (RI, Jennerjahn and Ittekkot, 1997, 1999) is most suited to indicate the relative state of degradation of proteinaceous organic matter in fresh suspension and surface sediments. The RI is the ratio of the molar percentages of the aromatic amino acids (tyrosine + phenylalanine) divided by the molar percentages of non-protein amino acids (ß-alanine + g-aminobutyric acid). As the aromatic are among the easily degradable and the non-protein amino acids are least susceptible to degradation, high ratios indicate relatively fresh and low ratios indicate degraded organic matter. RI is high in the freshwater of the Yenisei River with values >20 (Fig. 3e). In the resuspension zones, where sediment of low RI (<5, Fig. 4d) is resuspended and mixed with the freshwater RI signal, a decrease of RI to values below 10 (Fig. 3a) is observed. Furthermore, the RI in the surface layers of the mixing zones (10–20) is somewhat lower compared to the riverine freshwater, probably by the degradation of organic matter. At about 73°N, surface water RI abruptly increases to values >20 in the upper layers, revealing production of fresh marine organic matter which is consistent with enhanced percentages of POC and PN in this area.

4.3. Inorganic proxies

Inorganic proxies of the Yenisei River were already studied by Beeskow and Rachold (2003). In this study, we compare these earlier results with the organic proxies to better understand the processes in the mixing zone. The behaviour of manganese and iron as redox- and salinity-sensitive proxies was investigated in the Yenisei River transect. In order to avoid concentration-dependent effects, Mn/Al and Fe/Al ratios were used for particulate matter and surface sediments. Dissolved manganese and iron, in contrast, are given in concentrations.

In suspended matter, Mn/Al is rather constant in the freshwater part of the Yenisei River. A maximum of Mn/Al occurs with the increase in salinity (Fig. 6a). Depletion takes place in the area characterized by resuspension. In the Kara Sea suspension, Mn/Al is higher than in the freshwater part of the river. Dissolved manganese concentration is low (below detection limit) both in the freshwater part of the river and in the marine waters of the Kara Sea. It is significantly higher near the river bottom in the mixing zone. Sediment cores from the mixing zone show characteristics of anoxia in the sediment while the overlying water column is oxic. The high concentration of dissolved manganese near the bottom in the mixing zone most likely can be ascribed to early diagenetic release of reduced manganese into the overlying water column. As the water column is oxic in contrast to the sediment (benthic fauna is sparse, but existent; H. Deubel (AWI Bremerhaven), pers. comm.), the dissolved manganese is readily re-oxidized and removed from the dissolved phase.

Similar to Mn/Al, Fe/Al in suspended matter decreases in the mixing zone (Beeskow and Rachold, 2003). Nevertheless, the Fe/Al ratio starts to decrease at lower salinities than Mn/Al, but changes in Fe/Al are small compared to Mn/Al changes. Both Mn/Al and Fe/Al are depleted in the centres of resuspension, most likely due to dilution with suspended sediment of lower Mn/Al and Fe/Al, respectively. Dissolved iron is observed only in the southernmost part of the river at salinities of 0, most probably originating from the surrounding soils (Lisitsyn, 1995). As soon as the salinity is above 0, dissolved iron is coagulating and scavenged as Fe-oxyhydroxides from the water column, and concentrations drop below detection limit (Chester, 1990; Beeskow and Rachold, 2003).

At low salinities and within the mixing zone, primary productivity is of minor relevance due to low light penetration. In areas where photosynthesis is higher, biological processes interfere with the pure chemical and physical processes. In the area north of 73°30′N (which is some 600 km off the estuary), enhanced Mn/Al and Fe/Al ratios can be ascribed to the production of fresh marine organic material. Iron and manganese are analyzed in phytoplankton (Martin and Knauer, 1973), as iron in particular is important for the function of photosynthesis in phytoplankton (Tung-Yuang et al., 2003). Therefore, these elements are enriched in the suspended matter in the upper water column north of 73°30′N as the fresh marine organic material (phytoplankton) forms part of the suspended load.

4.4. The "marginal filter" of the Yenisei River

In general, the organic and inorganic constituents are influenced in different ways by the marginal filter: some (dissolved and particulate) constituents are only

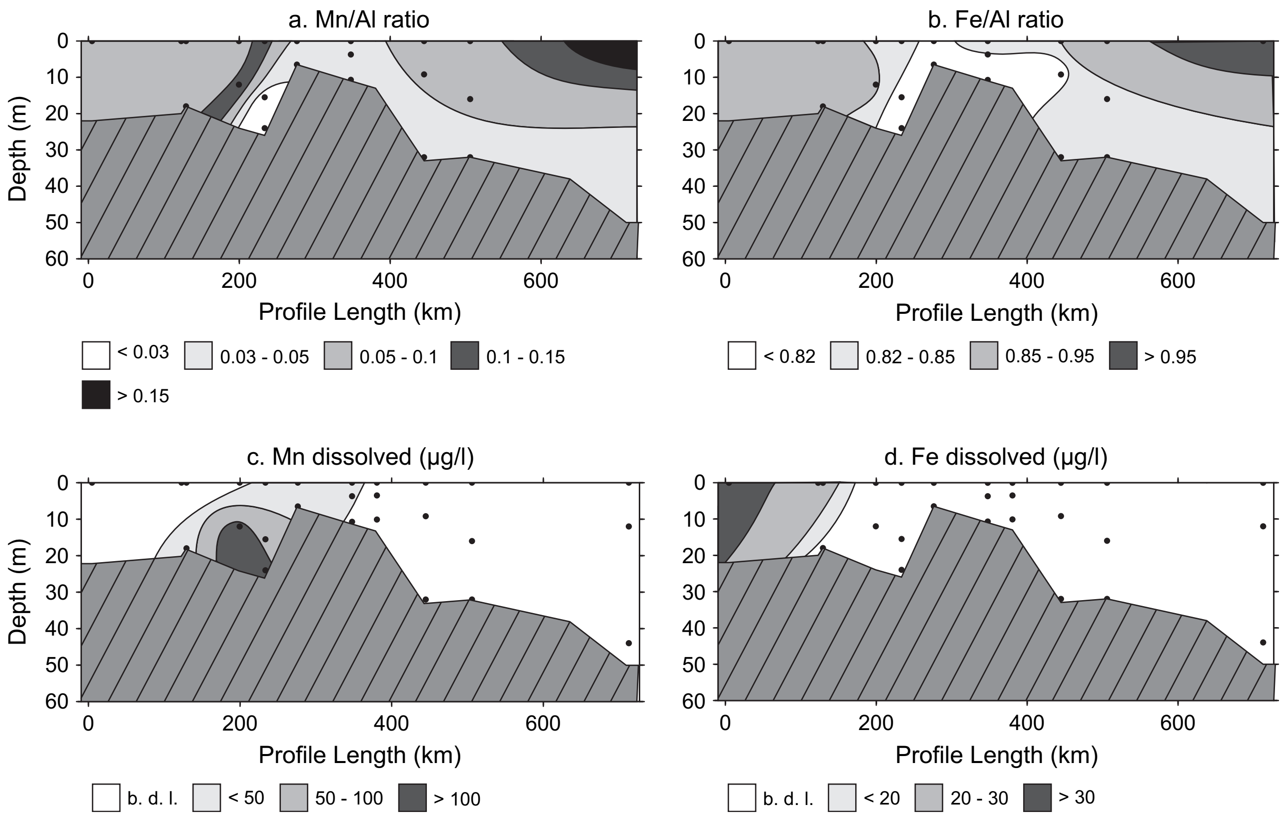

Fig. 6. Inorganic proxies profiles. (a) Mn/Al of particulate matter, (b) Fe/Al of particulate matter, (c) dissolved Mn (µg/l), (d) dissolved Fe (µg/l). Dots mark sampling points.

influenced by physical processes as dilution with other water masses and resuspension; some constituents are subject to chemical processes within the mixing zone.

In our study, bulk PN and POC are subject mainly to physical processes. Their percentages differ only (a) when they are mixed with saline marine water with lower POC and PN contents; and (b) due to changes in hydrography causing resuspension of surface sediment with lower TOC and TN content. However, even though percentages of suspended organic matter do not change within the mixing zone, organic matter is affected by degradation, as revealed by the RI. This degradation takes place exactly in the mixing zone at salinities above 0 but below 20. Köhler et al. (2003) report an almost conservative behaviour of dissolved organic carbon; the conservative behaviour of particulate organic matter found in this study further confirms the findings of Köhler et al. (2003) that interaction between dissolved and particulate phases of organic matter is quantitatively insignificant. Degradation of organic matter seems to affect its composition only.

TSM is affected by flocculation processes due to changing salinity, increasing its settling speed with increasing flocculation. At low salinities just above 0, flocculation is initiated (Fig. 2a and c). At salinities higher than 20, dilution of TSM due to mixing with marine water of lower TSM concentration is observed and the TSM concentration behaviour is conservative (Gebhardt et al., 2004). Flocculation produces large flocs with high settling rates; due to changing conditions in shear, these flocs tend to break once they reach the river bottom and are readily resuspended, forming part of the turbidity maximum (Kranck, 1984).

Dissolved iron is observed only in the freshwater part of the Yenisei River with concentrations of up to 35 µg/l (average concentration in rivers: 40 µg/l; Haese, 2000, and references therein). At the interface between pure freshwater and brackish water, dissolved iron precipitates as iron oxyhydroxides due to increasing destabilization of the mixed iron oxides-humic matter colloids (Sholkovitz, 1978), and is scavenged from the water column. The marginal filter thus acts as a sink for iron, which has been observed also in other studies (Sharp et al., 1984; Dai and Martin, 1995).

Mobilization of species formerly adsorbed to particulate matter was not observed in the mixing zone. However, mobilization of manganese takes place in the anoxic sediments underlying the mixing zone. This is reflected in enhanced dissolved manganese concentrations in this area. As the water column is – at least temporarily – oxic even above the anoxic sediment – in contrast to what has been assumed by Beeskow and Rachold (2003) – manganese is soon re-oxidized and scavenged from the water column. Nevertheless, this scavenging is not observable as the dilution of particulate Mn/Al by resuspension is superimposed. Mobilization of dissolved iron from the anoxic sediment is not observed. This can be explained by the fact that manganese is more mobile and more slowly oxidized than iron and, therefore, migrates more easily. Iron, in contrast, is more readily deposited. The redox potential of the Yenisei River mixing zone sediments allows manganese to be reduced and released into the water column, whereas iron is oxidized before entering the water column. This leads to a cycling of reduced and oxidized manganese.

4.5. Comparison with other marginal filter studies

4.5.1. Comparison with earlier studies from the Yenisei River

Many studies on proxies potentially affected by the changing conditions in the marginal filter have been carried out in the Yenisei River (e.g. Dai and Martin, 1995; Gurevich et al., 1995; Kravtsov et al., 1995; Kuptsov et al., 1995; Lebedeva and Shushkina, 1995; Lisitsyn et al., 1995; Makkaveev, 1995; Lukashin et al., 1999; Schoster et al., 2000; Paluszkiewicz et al., 2001), but in many cases the spatial distribution of data is too small to define the processes and interactions. A detailed study on inorganic proxies was carried out by Beeskow and Rachold (2003) forming the basis of our inorganic data set. Considering not only inorganic but additionally organic proxies and biological data, we agree with their findings about processes taking place in the mixing zone between riverine and marine water. Only for manganese, we propose a slight modification of their conclusion: Beeskow and Rachold (2003) conclude that the dissolved manganese maximum in the near-bottom layer of the mixing zone results from dissolution of suspended manganese due to anoxic or suboxic water. Even though there is evidence of low oxygen concentrations (<4 mg/l) as well as low pH and high ammonium values during an earlier cruise (Kravtsov et al., 1995), we think that the water is not totally anoxic (benthic fauna is sparse in this area, but existent; H. Deubel (AWI Bremerhaven, Germany), pers. comm.). The dissolved manganese most probably has its origin in the anoxic sediments and not in the water column.

A more general study was carried out by Lisitsyn (1995), describing the marginal filter of the world's rivers with special emphasis on the marginal filter in the Ob and Yenisei rivers as examples of Arctic rivers. Extremely high fluxes of TSM are reported (1321 and 22,156 mg m^{-2} d^{-1} for the Ob and Yenisei rivers, respectively; Lisitsyn et al., 1995), resulting in fluxes within marginal filters that are higher than those outside by factors of 100–1000 (Lisitsyn, 1995). In a worldwide compilation, about 90–95% of the suspension discharged by rivers into the mixing zone, 80% of the dissolved and 90% of the suspended iron and about 20% of the dissolved manganese do not reach the pelagic zone (Lisitsyn, 1995). However, the marginal filter of Arctic rivers behaves differently due to the strong seasonality of these rivers: the spring/summer period with the main river runoff has a time span of around 4 months, and only during this short time span, the marginal filter is comparable to rivers in lower latitudes. During the long autumn/winter period, only small amounts of river runoff are released into the Kara Sea, and, furthermore, the rivers and the adjacent Kara Sea are ice-covered. The ice cover prevents the water column from mixing, allowing the winter runoff to spread and distribute its suspension load widely (Lisitsyn, 1995). Additionally, high saline brines are formed during ice production. These brines sink to the Kara Sea floor due to their high density and transport the marginal filter material along the channel incisions towards the Arctic Ocean (Lisitsyn, 1995).

Lisitsyn (1995) observed two "plugs" within the marginal filter: a "silt plug" at salinities around 2 where flocculation and coagulation of clay, organic acids and iron coincide in space, and an "elementorganic plug" at salinities around 5 due to flocculation of organic matter and oxyhydroxides. In our study, iron precipitates at low salinities just at the beginning of the marginal filter, and TSM has its maximum flocculation at slightly higher salinities. Particulate manganese maximum is found at even higher salinities than the TSM maximum concentrations. The flocculation of organic matter as postulated by Lisitsyn (1995) to occur at salinities around 5 was not observed in our study.

Lisitsyn (1995) proposes that the main part of dissolved manganese (about 80%) escapes the marginal filter. The riverine input of dissolved manganese into the marginal filter of the Yenisei River is small (i.e. below detection limit), and so is the output into the Kara Sea. We, therefore, cannot estimate the amount of dissolved manganese that escapes the marginal filter; we only observe that the manganese released into the water column within the marginal filter zone does not leave it. Nevertheless, we notice that – even though the dissolved manganese concentrations are below detection limit in the riverine freshwater, precipitation of dissolved manganese occurs at low salinities as revealed from higher Mn/Al in the suspended matter.

For many proxies, we agree with the definition of the marginal filter sensu Lisitsyn (1995). However, not all postulated processes are observed in the Yenisei River: particulate organic matter behaves rather conservatively even though degradation occurs within the mixing zone. Furthermore, not all processes result from changes in salinity: flocculation of particulate matter is also induced by changing hydrographic conditions (e.g. Burban et al., 1989, 1990; Lick et al., 1993; Winterwerp, 2002), and the release of dissolved manganese within the mixing zone originates from redox processes within the anoxic sediment.

4.5.2. Comparison with other rivers

4.5.2.1. Lena River (Siberia). The Lena River drains into the Laptev Sea (Siberia) and is comparable to the Yenisei River in its size and geographical position. However, the Lena River forms a delta with several distributaries and islands in contrast to the Yenisei River characterized by an estuary. Gordeev and Shevchenko (1995) found conservative behaviour of iron and some trace elements in the mixing zone, indicating a low affinity for biogenic matter. Nevertheless, the small data set does not allow a reliable conclusion. However, the data set of Cauwet and Sidorov (1996) does not show any evidence for consumption of POC on its way through the marginal filter. The authors assume that only a small part of the terrestrial POC undergoes degradation whereas the marine POC is recycled almost in situ. This is quite similar to the conservative behaviour of POC observed in the Yenisei River. Conservative behaviour was also postulated for the Lena River DOC (Cauwet and Sidorov, 1996) similar to the study on the Yenisei River DOC (Köhler et al., 2003).

4.5.2.2. St. Lawrence River (North America). The St. Lawrence River consists of a series of banks, channels and basins, with water depths reaching 150 m in the deepest basin. The turbidity maximum of the upper St. Lawrence River is a prominent feature of about 180 km length and 2–24 km width (Gobeil et al., 1981). Non-conservative behaviour of dissolved Fe (removal) and dissolved Mn (input from sediment) was observed by Bewers and Yeats (1978, 1979) similar to our observations in the Yenisei River. Furthermore, lower content of e.g. Mn in the particulate matter was observed and interpreted as desorption by Cossa and Poulet (1978). Gobeil et al. (1981) observed decreasing Mn/Al ratios at the landward end of the turbidity front, being not related to salinity as this feature was found also when the turbidity maximum occurred in freshwater. Nevertheless, this feature was also not related to TSM concentrations as it was very stable throughout the tidal cycle with differing TSM concentration (10–220 mg/l over the observed tidal cycle). Gobeil et al. (1981) pointed out that the Mn/Al ratio was influenced by bottom processes, being frequently higher in near-bottom samples than at the surface. Furthermore, Fe/Al decreased in the turbidity zone and did not reflect the addition of Fe to the solid phase by the precipitation of dissolved iron. Gobeil et al. (1981) and Hamblin (1989) showed (a) that salinity fluctuations were not the main process causing the distinct changes in geochemical composition of dissolved and particulate matter in the turbidity maximum; and (b) sedimentological and hydrological processes to be much more important. In our study, differentiating salinity-driven from processes driven by hydrology and sedimentation is not easy. Nevertheless, we showed that resuspension due to changes in hydrological conditions plays an important role in the Yenisei River.

Lucotte (1989) investigated the particulate organic matter in the upper St. Lawrence estuary, and found (a) a perfect dilution line between the riverine and the marine $\delta^{13}C$ pool, pointing at both a negligible influence of estuarine bioproduction and a negligible geochemical transformation of POC; and (b) a residence time of POC of about 6–12 months of the particles already in suspension with a slow replacement by new particles. Similarly, Yenisei River POC shows conservative behaviour.

4.5.2.3. Changjiang (=Yangtze) River (China). The Changjiang River is the fourth largest river in terms of sediment discharge and average water discharge with a large intraseasonal and interannual variability (Milliman et al., 1985, and references therein). The river is characterized by a mesotidal, partially mixed estuary divided by islands into several branches and arms and finally opening into four mouths. The turbidity maximum in the Changjiang River is fed by resuspension and erosion of the river bed (Jiufa and Chen, 1998). Settling velocities of the suspended matter is increased due to flocculation, and during periods of weak tidal currents the massive settling often gives rise to formation of fluid muds. Jiufa and Chen (1998) carried out a lab experiment on the flocculation of suspended matter in the Changjiang River, showing that the flocculation of different particle sizes depends on the flow velocity of the water. It is likely that at a certain flow velocity a certain grain size starts to flocculate, what might result in a maximum turbidity area and even in fluid mud layers due to changes in hydrography without changes in salinity. The authors further showed that the occurrence of the turbidity maximum in the deep layer normally is associated with the reversal of the tidal currents. An area of zero net transport and, therefore, accumulation was detected as a combined effect of tidal asymmetry, runoff and density circulation. Jiufa and Chen (1998) point out that the major processes favouring the transport of suspended matter consist of tidal pumping and advective terms.

It is likely that even in the Yenisei River, flocculation occurs at zones where the velocity is favourable for certain grain sizes. Nevertheless, accumulation of sediment does not take place in the same area as flocculation; the thick sediment packages most probably are laid down in an area of zero net transport as in the Changjiang River.

Cauwet and Mackenzie (1993) carried out a study on organic matter in the Changjiang River. They show that DOC is not influenced by salinity as in the Yenisei River, but in contrast to what was found in the Yenisei River, DOC is sometimes enhanced in the near-bottom layer in the Changjiang River. This was interpreted to occur due to resuspension of interstitial water enriched in DOC.

5. Conclusion

In this study, we focused on the summer situation in the Yenisei River mixing zone. Flocculation and resuspension of particulate matter was observed in the mixing zone, forming the maximum turbidity zone, which in turn enhances the flocculation processes due to higher concentrations of particles (e.g. Burban et al., 1989, 1990; Lick et al., 1993). Resuspension was observed in areas of changing hydrographic conditions, and it mainly affected the near-bottom layers. Organic suspended matter (POC, PN) percentages are only influenced by sedimentological and hydrographical processes (dilution, resuspension) even though POC and PN undergo degradation as revealed by amino acid data. As shown by Köhler et al. (2003), dissolved organic carbon (DOC) also behaves conservatively, by supporting the observed conservative behaviour of suspended organic matter and the fact that suspended and dissolved organic matter do not interact considerably in the Yenisei River marginal filter.

Non-conservative behaviour was observed considering the redox- and salinity-sensitive elements (Fe, Mn). Dissolved iron is scavenged from the water column at the landward edge of the mixing zone. A decrease in Fe/Al is observed in the mixing zone and can be ascribed to resuspension of sediment with lower Fe/Al ratio. Dissolved manganese concentrations are below detection limit in the freshwater of the Yenisei River. At the landward edge of the marginal filter, however, Mn/Al increases due to adsorption of the sparse dissolved manganese present in the freshwater. Within the mixing zone, however, Mn/Al is depleted similarly to Fe/Al due to resuspension. Dissolved manganese is largely enhanced in the near-bottom layers within the maximum turbidity zone, which can be ascribed to release of reduced manganese from anoxic sediments into the water column. This process may be enhanced due to resuspension of sediment and associated interstitial water with enhanced dissolved manganese concentrations.

Fe/Al and Mn/Al as well as POC and PN are high in the marine surface waters of the Kara Sea. We propose that this is due to the enhanced production of marine organic matter in this area; this has also been revealed by biological data (e.g. Nöthig et al., 2003) as well as by amino acid proxies (Unger et al., 2005).

Differentiation of processes causing the observed effects in the maximum turbidity zone is not always clear in the Yenisei River. Resuspension of bottom material takes place due to hydrological changes in the river flow, and the mobilization of dissolved manganese in the near-bottom layers in the marginal filter is caused by reducing conditions in the sediment. However, precipitation of dissolved iron at the landward edge of the mixing zone as well as the increase of Mn/Al in suspended matter of the same zone is induced by increasing salinity.

Altogether, the summer situation of the Yenisei River marginal filter compares well to other rivers. However, for better differentiation between the processes taking place in the marginal filter of the Yenisei River, a better spatial and temporal resolution, e.g. during a full tidal cycle and during winter conditions, is needed.

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