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Decreased silica land–sea fluxes through damming in the Baltic Sea catchment – significance of particle trapping and hydrological alterations

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Abstract. We tested the hypothesis that reservoirs with low water residence time and autochthonous production influence river biogeochemistry in eutrophied river systems draining cultivated watersheds. The effect of a single artificial water reservoir and consecutive reservoirs on silica (Si) river fluxes is exemplified by the moderately dammed Vistula River and the heavily regulated Daugava River that are compared with the practically undammed Oder River. The sum of the discharge weighted annual mean biogenic silica (BSi) and dissolved silicate (DSi) concentrations in the rivers Oder, Vistula and Daugava were about 160 μM (40 + 120 μM), 150 μM (20 + 130 μM) and 88 μM (6 + 82 μM), respectively. Assuming BSi and DSi concentrations as observed in the Oder River as typical for eutrophied but undammed rivers, complete trapping of this BSi could have lowered Si fluxes to the Baltic Sea from rivers with cultivated watersheds by 25%. The superimposed effect of hydrological alterations on reduced Si land–sea fluxes is demonstrated by studies in the boreal/subarctic and oligotrophic rivers Kalixälven and Lueälven. The DSi yield of the heavily dammed Luleälven (793 kg km^{-2} yr^{-1}) constituted only 63% of that was found in the unregulated Kalixälven (1261 kg km^{-2} yr^{-1}), despite the specific runoff of the Luleälven (672 mm m^{-2} yr^{-1}) being 19% higher than that of theKalixälven (563 mm m^{-2} yr^{-1}); runoff normalized DSi yield of the former, regulated watershed, was only half the DSi yield of the latter, unperturbed watershed. Based on these findings, it is hypothesized here that perturbed surface water–groundwater interactions are the major reasons for the reduced annual fluctuations in DSi concentrations as also seen in the heavily dammed and eutrophic river systems such as the Daugava and Danube.

Introduction

A series of studies have shown that hydrological alterations have decreased the dissolved silicate (DSi) loads to the sea with adverse effects on the marine ecosystem (Conley et al. 1993; Garnier et al. 1999; Humborg et al. 2000, 2002). This has also been shown for the land–ocean continuum Iron Gate I and II–Lower Danube–Black Sea (Humborg et al. 1997), and the effects are often easier to observe in inland seas with long water residence times. Even in the Baltic Sea decreasing DSi trends have been shown (Rahm et al. 1995) and it was assumed that marine eutrophication was the primary reason for the decline in DSi concentrations. In fact, more recent findings suggested that regulated rivers draining into the Gulf of Bothnia, the northern part of the Baltic Sea, have much reduced DSi loads and may significantly contribute to the DSi decline in the Baltic Sea (Humborg et al. 2000). It has been shown that DSi weathering fluxes were much lower in the regulated boreal river systems (Humborg et al. 2002), but the overall effect on DSi land–sea fluxes was not well quantified, since these studies were focused on time and space patterns of DSi concentrations, but not on yields. For the southern eutrophied river systems of the Baltic Sea catchment, no studies on the effect of damming on Si fluxes exist at all.

In general, the boreal/subarctic rivers entering the Gulf of Bothnia have a higher specific runoff, especially the northern Swedish rivers which have a steeper catchment slope compared to the rivers draining the southeastern catchments of the Baltic Sea. Damming is much more frequent in the boreal rivers owing to its higher effectiveness in terms of power generation; major reservoirs located in the headwaters can hold between 30 and 70% of their annual water discharge (Dynesius and Nilsson 1994). In contrast, damming is much less frequent in the low-land rivers of the southeastern catchment of the Baltic Sea and mostly minor dams and reservoirs, with short water residence times, were built there. The effect of such dams with short residence times – though many of them are indicated as large dams by the International Commission on Large Dams (ICOLD) that defines the magnitude of dams by height of the dams – on Si land–sea fluxes have recently been questioned. Friedl et al. (2004) concluded that the water residence time of about one week in the Iron Gate I reservoir along the Danube is simply not long enough to allow the development of massive diatom blooms and hence cannot be the cause for the observed DSi decline in the Black Sea as reported by Humborg et al. (1997). In fact, the 'artificial lake effect' (van Bennekom and Salomons 1981), i.e., the removal of nutrients in the reservoir sediments, and hereafter referred to as the particle trapping effect, was thought to be mainly caused by autochthonous diatom blooms in the reservoirs. Therefore, the question arises whether reservoirs with low water residence times, and hence low autochthonous production, will significantly influence river biogeochemistry.

To answer this question, we sampled DSi and biogenic silica (BSi) in eutrophied watersheds of the Baltic Sea with various degrees of damming; hence, emphasis was given to the particle trapping effect. The contribution of BSi, carried by rivers in suspension, has proven to be a significant component in the world's ocean Si budget (Conley 1997), but seasonal data are scarce (Admiraal et al. 1990). However, there are a few European rivers draining cultivated watersheds, such as the Oder River in Poland, that remained practically undammed (*sensu* Dynesius and Nilsson 1994). We compared the Oder River with the moderately dammed Vistula River and the heavily dammed Daugava River (Figure 1), all characterized by a similar eutrophication status and by similar geological and climatic settings. The seasonal pattern of the DSi concentrations is compared with those in the rivers Kalixälven (unperturbed)

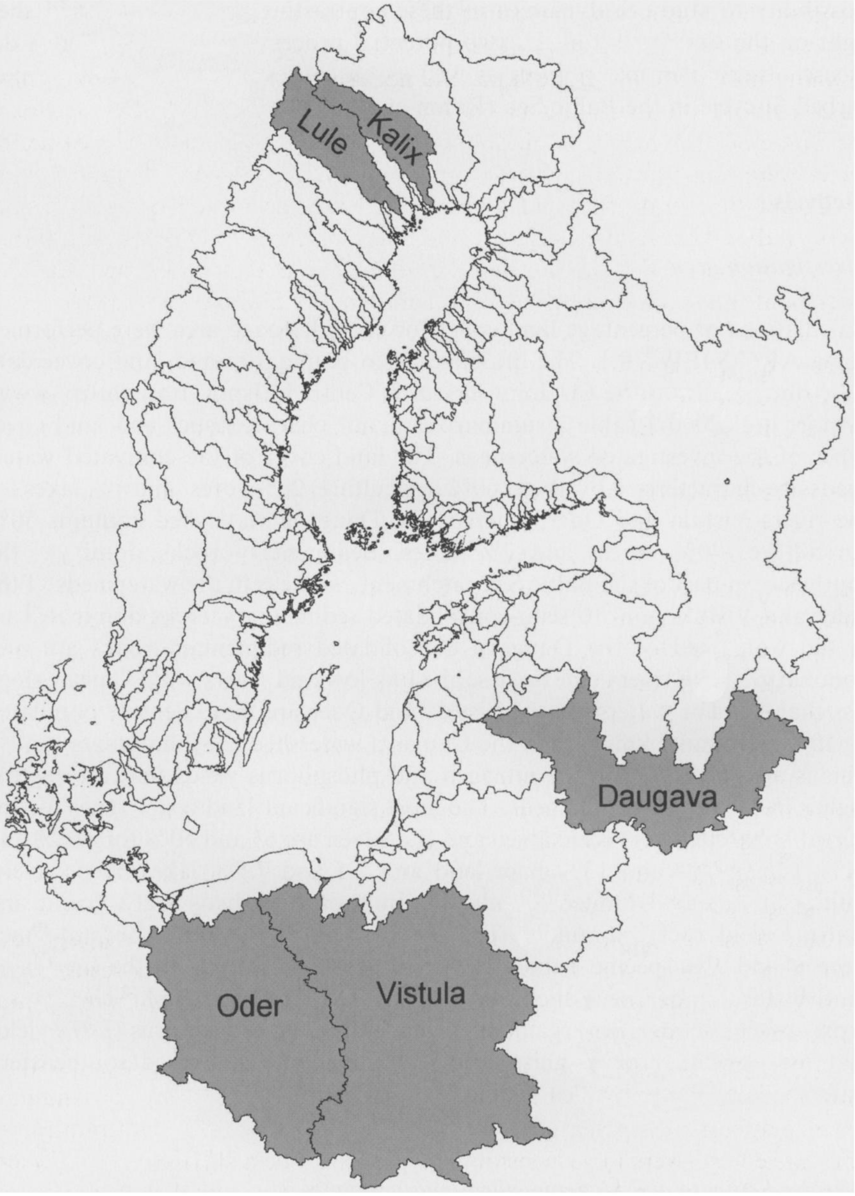

Figure 1. Baltic Sea catchment and the location of investigated watersheds.

and Luleälven (heavily dammed), draining into the Gulf of Bothnia (Figure 1). Since these rivers are extremly oligotrophic, the effect of hydrological alterations – though much more drastic as compared to the southeastern rivers, can be studied as such, and disentangled from the particle trapping effect. Thus, the possibility to study Si dynamics in these contrasting environments will shed light on the significance of the two potential processes responsible for Si decrease observed in many rivers as well as on causes responsible for the perturbed Si cycle in the Baltic Sea (Rahm et al. 1995).

Methods

Investigation area

Calculations of percentage land cover for each drainage area were performed using ARC VIEW® 8.1. The drainage basin boundaries and land cover data were obtained from the EU Joint Research Centre in Ispra, Italy (http://www-gvm.jrc.it/glc2000). Table 1 summarizes major characteristics and land cover types of the investigated watersheds. The land cover of the cultivated watersheds are characterized by about 60% agriculture, 20% forest and 1% lakes for the rivers Vistula and Oder, whereas the Daugava watershed contains 50% agriculture, 40% forest and 2% lakes. Sedimentary rocks dominate the southeastern part of the Baltic Sea catchment, whereas in the watersheds of the Oder and Vistula non- to semi-consolidated sedimentary rocks dominate and in the watershed of the Daugava consolidated sedimentary rocks are predominating. The rivers can be described as lowland rivers with a mean slope less than 1°. The watersheds of Vistula and Oder are more densely populated (> 100 inhabitants km^{-2}) than the Daugava watershed (33 inhabitants km^{-2}). This is also expressed in the nitrogen and phosphorus yields that are slightly higher in the former watersheds. The most significant land cover types for the boreal/subarctic rivers Kalixälven and Luleälven are 65 and 50% forest, 20 and 14% wetlands, 4 and 13% bare land and 2.5 and 7.5% lakes, respectively. Cultivated areas are limited to only 1%. In both watersheds acid volcanic and plutonic acid rocks dominate. The mean slope of the watersheds is much steeper and the specific runoff is two times higher than in the cultivated southeastern watersheds which were investigated. The oligotrophic character is expressed by dissolved inorganic nitrogen (DIN) and phosphorus (DIP) yields that are one order of magnitude lower than in the cultivated southeastern watersheds of the Baltic Sea (Table 1).

Dissolved silicate and biogenic silica measurements

We carried out biweekly BSi and DSi measurements in the rivers Oder and Vistula over the period April 2003 and July 2004, and for the Daugava River between April 2003 and April 2004; all sampling locations were situated near the river mouths. DSi was determined after the method described by Koroleff (1983) and BSi following the method of DeMaster (1979). Since 1970, the rivers Kalixälven and Luleälven have been routinely monitored (monthly) for DSi at

Table 1. Landscape characteristics and nutrient yields of the investigated watersheds.

	Catchment area (km^2)	Mean slope (°)	Mean temp (°C)	Pop. density (Inh. km^{-2})	Deciduos (%)	Coniferous (%)	Mixed forest (%)	Herbaceous (%)	Wetlands (%)	Cultivated (%)	Bare (%)	Water (%)	Snow and ice (%)	Artificial (%)	Runoff (km^3 yr^{-1})	Spec. runoff (mm m^{-2} yr^{-1})	DIN yield (kg km^{-2} yr^{-1})	TN yield (kg km^{-2} yr^{-1})	DIP yield (kg km^{-2} yr^{-1})	TP yield (kg km^{-2} yr^{-1})	DSi yield (kg km^{-2} yr^{-1})
Luleälven	24934	3.4	−0.1	1.2	3.8	35.1	9.1	14.5	14.6	0.9	13.3	7.4	1.2	0.1	16.7	672	30	136	1.6	7.1	793
Kalixälven	17673	1.9	−0.5	2.0	3.0	43.0	19.1	7.1	20.3	1.2	3.5	2.5	0.2	0.1	10.0	563	47	202	2.1	13.3	1261
Daugava	85852	0.3	5.6	33	5.9	17.3	16.7	5.9	0.5	51.4	0.0	1.7	0.0	0.6	21.1	245	295	456	10.7	14.9	411
Vistula	192899	0.7	7.6	121	2.9	11.4	7.2	11.6	0.5	64.3	0.0	0.8	0.0	1.2	33.6	189	426	639	20.5	31.8	768
Oder	117589	0.6	8.2	138	0.8	15.6	7.4	8.9	0.6	64.2	0.0	0.8	0.0	1.8	16.9	141	435	628	19.6	53.8	525

their mouths, by the Swedish University of Agricultural Sciences (SLU, Department of Environmental Assessment).

To compare DSi yields of the studied watersheds we used as long time records as possible. For the watersheds of the Daugava, Luleälven and Kalixälven there were available monitoring data for the years 1970–2000; for the watersheds of the Oder and Vistula we used the time period 2000–2004. Note, that discharge weighted annual mean DSi concentrations for the southeastern rivers were calculated for a longer period, therefore they may slightly differ when referred to the detailed DSi *vs.* BSi measurements conducted in 2003–2004.

Results

Cultivated agricultural watersheds

In the Oder River, discharge weighted mean annual BSi concentrations were 40 μM for the period April 2003 to March 2004, which corresponded to ca. 6% of total suspended sediment (TSS; long-term mean of 22 mg l^{-1}) concentration in this river. Highest BSi concentrations, reaching $\sim$100 μM, were found during the growth season, when DSi was at its minimum and, thus, they most probably originated from diatom frustules (Figure 2a). Note, that during periods of the growth season, DSi concentrations in both rivers were depleted (Figure 2a and b). The discharge weighted mean annual DSi concentration in the Oder River amounted to 120 μM for the same time period. The discharge weighted mean annual DSi concentration (130 μM) in the Vistula River did not differ very much from the value obtained for the Oder River and the seasonal cycle almost mirrored that of the undammed Oder River (Figure 2b). However, the discharge weighted mean annual BSi concentrations in the Vistula River (20 μM) were two times lower than those in the waters of the Oder River. The differences in DSi yields (Table 1), at comparable DSi concentrations, of the Oder River (525 kg km^{-2} yr^{-1} and 133 μM) and the Vistula River (768 kg km^{-2} yr^{-1} and 145 μM) can be mainly attributed to differences in their specific runoffs; the specific runoff in the watershed of the Vistula River (189 mm m^{-2} $yr^{-1)}$ was by about 25% higher than in the watershed of the Oder River (141 mm m^{-2} yr^{-1}).

The Vistula River has been moderately dammed in Włocławek since 1970 with a total volume and surface area equal to 0.41 km^3 and 70.4 km^2, respectively. About 1.7 million m^3 yr^{-1} of sediments accumulate in this reservoir (Anon. 2001) reducing the TSS concentration by ca. 50 mg l^{-1}. This estimate is in good accordance with historical measurements indicating TSS concentrations of ca. 75 mg l^{-1} in the Vistula River before damming (Milliman et al. 1995), in contrast to the mean concentrations of 17 mg l^{-1}found in the 90s. This gives a sedimentation rate of about 2 $cm^{-1}yr^{-1}$, if we assume that all material is evenly distributed over the reservoir area with a bulk density of

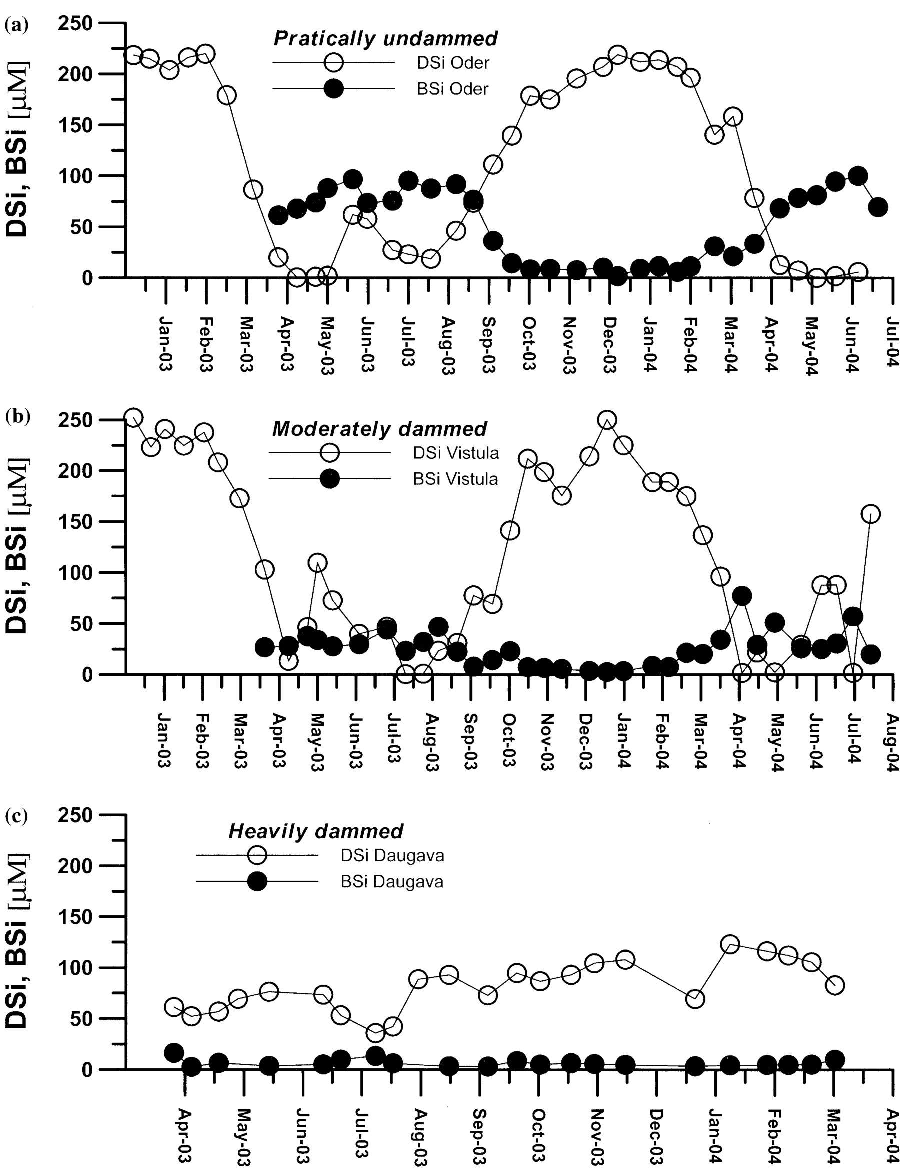

Figure 2. Dissolved silicate (DSi) and biogenic silica (BSi) concentrations measured at the mouth of the rivers Oder (a), Vistula (b) and Daugava (c).

1000 kg m^{-3}. Water residence time in the Vistula reservoir are about 1 day, thus, massive diatom blooms are not very likely to occur.

The Daugava River was heavily dammed in the 1970s and the following three major reservoirs were erected: near Riga (total volume of 0.34 km^3), Kegums (total volume of 0.16 km^3) and Plavinas (total volume of 0.51 km^3); water residence time in each reservoir is about 6, 3 and 9 days, respectively. Unfortunately, we have no sedimentation records in these reservoirs, but our measurements at the river mouth revealed a mean TSS concentration of only 4 mg l^{-1}. The discharge weighted mean annual BSi concentrations in the Daugava River (Figure 2c) were also the lowest (6 μM) among the rivers studied, but interestingly, also the discharge weighted mean annual DSi concentration (82 μM) was lower as compared to the rivers and Oder and Vistula. DSi yields calculated for the period 1970-2000 (411 kg km^{-2} yr^{-1}) were even lower than those in the Oder and Vistula watersheds, although the specific runoff of the Daugava watershed (245 mm m^{-2} yr^{-1}) was about 30 and 74% higher, respectively, than in the former two watersheds. Runoff normalized DSi yield of the Daugava watershed was only 45 and 42%, respectively, of the DSi yields calculated for the watersheds of the Oder and the Vistula.

Boreal/subarctic watersheds

Discharge weighted mean annual DSi concentration in the unperturbed Kalixälven (81 μM) was about twice as high as in the heavily dammed Luleälven (41 μM), whereas the DSi yield of the latter (793 kg km^{-2} yr^{-1}) was only 40% lower compared to the Kalixälven (1261 kg km^{-2} yr^{-1}) due to a 19% higher specific runoff in the Luleälven (672 mm m^{-2} yr^{-1}) compared to the Kalixälven (563 mm m^{-2} yr^{-1}) (Table 1). Runoff normalized DSi yields were 53% in the former regulated watershed compared to the latter unperturbed watershed. Seasonal variations in DSi concentrations observed in the Kalixälven were much less pronounced in the heavily dammed Luleälven, and especially winter DSi maxima were much reduced (Figure 3b). This can be partly explained by a continuous water discharge generated by the power stations, namely Sitasjure, Akkajaure, Stora Lulevatten and Tjaktajaure, located in the headwaters of the Luleälven and emptying the four major reservoirs. All man-made reservoirs in the Luleälven have a capacity of ca. 11 km^3, corresponding to ca. 72% of the annual discharge of the Luleälven. With this reservoir life storage, the Luleälven became one of the heaviest regulated major rivers in the northern Eurasia (Dynesius and Nilsson 1994).

Discussion

Our study on Si fluxes in various regulated and unregulated rivers in the Baltic Sea catchment show that damming has a profound impact on Si fluxes and is not just restricted to diatom blooms in the reservoirs and subsequent nutrient removal in reservoir sediments. Minor dams and reservoirs have the potential to significantly impact river biogeochemistry due to the strong TSS and BSi trapping efficiency, and to altering flow regimes, especially in cases when

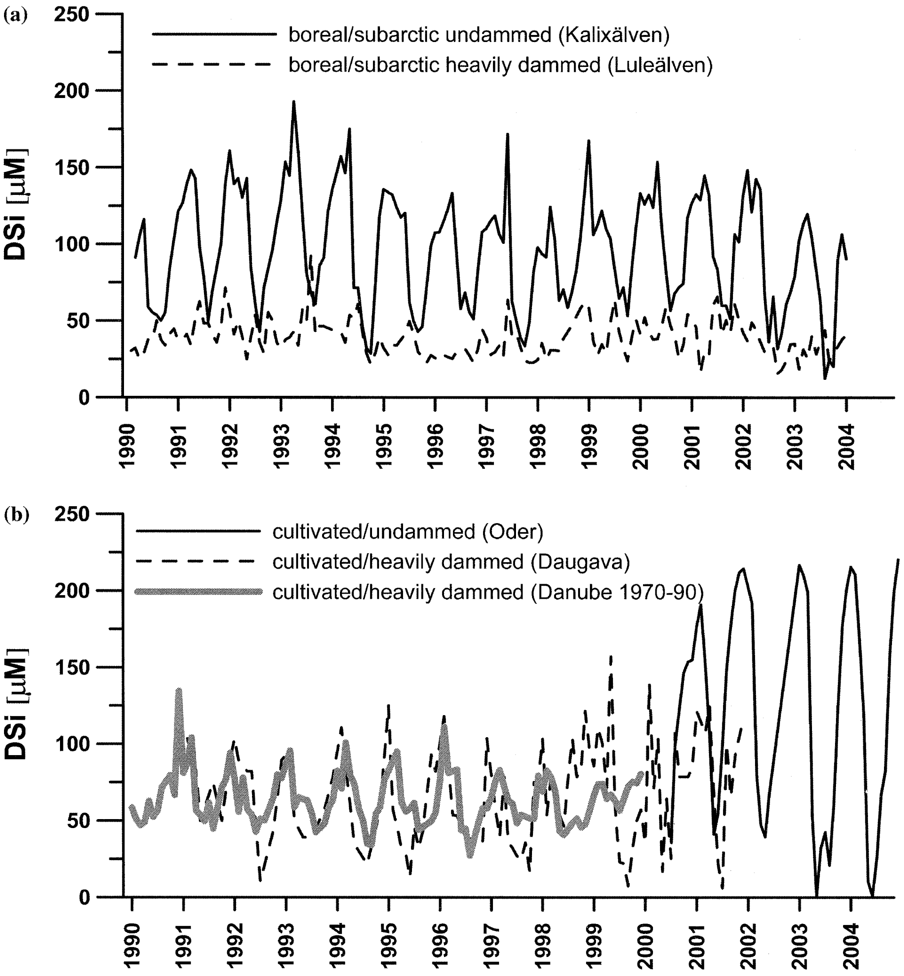

Figure 3. Dissolved silicate (DSi) concentrations measured at mouth of the rivers Kalixälven and Luleälven (a), Oder and Daugava (b); DSi concentrations in the rivers Daugava and Oder are compared with the long-term (1970–1992) DSi concentrations of the Danube River.

consecutive dams were built. These hydrological alterations apparently affect groundwater-surface water interactions, and by consequent lowering of Si weathering fluxes may serve as an additional and hitherto overlooked explanation for the lower DSi concentrations observed in all heavily regulated rivers of this study (eutrophic and oligotrophic), even during the unproductive winter season. These finding may have far reaching implications for understanding of the reduction in DSi concentrations observed in the major river systems such as the Mississippi River (Turner and Rabalais 2003) or the Changjiang River (Li and Cheng 2001) that can influence entire coastal seas by its altered nutrient compositions. Moreover, our study may also shed new light on the controversy that damming has lead to decreased Si transports by the Danube River into the Black Sea after the erection of the Iron Gate dams (Humborg et al. 1997), while a DSi input-output balance of the Iron Gate I based on data collected in 2001 has not shown a significant removal due to autochthonous diatom blooms (Friedl et al. 2004).

Trapping effect of reservoirs with low water residence times

Even one single reservoir with low water residence times, as in the case of the Vistula River, significantly reduced the BSi load. Consecutive dams, with similar low reservoir volumes, as in the case of the Daugava River, retain practically all BSi and also lower overall DSi concentrations. Although significant autochthonous production can be ruled out, due to the short water residence times of the order of days, these reservoirs retain efficiently BSi produced upstream and it is not of major importance where BSi has been produced. Assuming a discharge weighted mean BSi and DSi concentration of 40 and 120 μM, respectively, as observed in the Oder River, which might be taken as a reference for eutrophied but undammed rivers, a complete trapping of this BSi could have lowered Si fluxes to the Baltic Sea from rivers with cultivated watersheds by 25%. However, an even higher BSi production is conceivable in other eutrophied river systems, since diatoms appear to be DSi limited in both the Oder River and the Vistula River, since DSi concentrations fall below 2 μM during the growth season when most diatom become DSi limited (Egge and Asknes 1992).

Our study of the cultivated and eutrophied river systems of the southeastern Baltic Sea, varying from the undammed Oder River, through the moderately dammed Vistula River to the heavily dammed Daugava River allow to make a backward time projection of changes in DSi in major river systems such as the Danube River. The mean DSi concentration in the Danube River decreased from a pre-dam concentration of 140 μM for the year 1959 and 1960 (Almazov 1961) to a mean post-Iron Gates concentration of 60 μM in the 1970s and 1980s (Humborg et al. 1997). These values appear fully reasonable when compared with data from the practically undammed Oder River (mean DSi + BSi concentrations of 160 μM) and the heavily dammed Daugava River (mean DSi + BSi concentrations of 88 μM). Seasonal DSi cycle in the Danube River points to a significant biological production; the winter and summer values in the Iron Gate reservoirs reported for the year 2001 (Friedl et al. 2004), reach ca. 150 μM and <20 μM DSi, respectively; the average DSi concentration was about 80 μM. Assuming BSi discharge weighted concentration of 40 μM, i.e., comparable with that observed in the Oder River characterized by a similar eutrophication status, the burial of BSi could explain about half of the observed reduction of 80 μM after the erection of the Iron Gates.

We estimated a TSS loss in the Vistula River with 50 mg l^{-1}, that comes along with a retention of ca. 20 μM BSi removal. A much more significant trapping of BSi is conceivable for the Iron Gate reservoirs, taking into account the much higher sedimentation rates there. Significant impacts of the Iron Gates dams on decreasing sediment loads of the Danube River have been well investigated, since TSS have been monitored along various stations upstream and downstream of these dams for the past 130 years. The biggest dam along the Danube is the Iron Gate I (located at km 947), which created a reservoir of ca. 4 km^3 in volume (water residence time $\sim$7 days). Following the construction of the dam Iron Gate I the sediment discharge decreased by 30–40% at the nearest downstream station (Panin and Jipa 2002) and simultaneously the DSi winter concentrations declined sharply along the Romanian coast (Humborg et al. 1997). In 1984, a second dam, the Iron Gate II (located at km 864), was erected and a further drastic decrease in both the sediment discharge (by 60–70%; (Panin and Jipa 2002) and the DSi winter concentrations along the Black Sea coast was observed (Humborg et al. 1997). Panin and Jipa (2002) estimated that 20–30,000 kt yr^{-1} are retained behind the Iron Gate I, and an additional 20,000 kt yr^{-1} can be estimated for the Iron Gate II. BSi measurements from the Danube River are scarce and there are few numbers reported for June 1995 (Reschke 1999) and those indicate 1.9% of the TSS as BSi. This gives theoretically 800 kt yr^{-1} BSi removal in Iron Gates I and II, and that can be compared with the approximation made by Humborg et al. (1997) who estimated the overall DSi retention of both reservoirs to ca. 500–600 kt yr^{-1}.

Friedl et al. (2004) show that the Iron Gate I dam is nowadays a non-blooming area which made these authors question the role of the Iron Gates as a significant Si trap. In light of our present studies we are of the opinion that their conclusion might underestimate the effect of dams. By studying the undammed and dammed Baltic Sea rivers, we have proven that similar kinds of dams are efficient Si traps and there is no doubt that the Iron Gates must have been efficient traps, which is supported by the studies of Panin and Jipa (2002). More than 150 dams have been built along the Danube River since the 1970s (Raducu 2002), and these constructions must have lowered the upstream TSS and BSi concentrations. Friedl et al. (2004) also acknowledged that upstream dams must be responsible for the low DSi concentrations of the Danube River. A major player reducing significant amounts of TSS and BSi, is the largest engineering system along the Danube River in Gabcikovo at the Slovakian/Hungarian border (operating since 1992). Thus, the situation today cannot simply be compared with the situation in the 1970s when this first major dam in the Danube River, the Iron Gate I, was erected and a massive sedimentation took place. The past TSS and BSi concentrations can only be estimated by studying in detail the reservoirs' sediments. A simultaneous decrease in TSS and DSi loads has also been reported for the Changjiang River (Li and Cheng 2001) based on long-term records initiated in 1959, and a much more significant decrease in both TSS and DSi loads is anticipated now, after recent closing of the Three Gorges Dam.

In undammed rivers, the BSi is transported to the estuarine environment where freshwater diatoms die and re-dissolution of BSi is fast, as observed in many estuaries, including the Danube estuary (Ragueneau et al. 2002). In contrast, the process of re-dissolution of the BSi trapped behind dams is probably low, since burial rates in the reservoirs are estimated to be 6–80 times higher than in natural lakes (Dean and Gorham 1998). In the Iron Gate reservoirs a sedimentation rate could be in the order of 15 cm yr^{-1}, if we assume that 40,000 kt yr^{-1} TSS, with a bulk density of 1 000 kg m^{-3}, is evenly distributed over the area of both reservoirs (ca. 230 $km^{2)}$; similar assumptions suggest that the sedimentation rate in the Vistula reservoir in Włocławek were 2 cm yr^{-1}. Much more detailed studies on sedimentation rates behind dams are needed on a global scale and more exact knowledge on river sediment density and porosity are needed. However, these rough estimates clearly show that sedimentation rates behind dams are far from natural patterns and this has far reaching implications for re-dissolution patterns of BSi. As shown by Canfield (1993), at sedimentation rates of several g cm^{-2} almost all organic carbon becomes preserved, and diatom shells, that are coated with an organic layer (Bidle et al. 2002), should behave similarly. Moreover, Reschke et al. (2002) found an increasing amount (from 1.4 to 6.5%) of BSi in the surface sediments gathered at several stations distributed from the entrance to the Iron Gate I reservoir (km 1072) to a station near the dam (km 947). However, the different re-dissolution rates of BSi in reservoirs (probably negligible) and in estuaries (very fast) can explain why DSi reductions can be recorded at coastal stations off the river mouth so quickly after closing the dams (Humborg et al. 1997).

An unknown pool in the discussion of Si transport by rives is the role of non-diatom BSi, i.e., phytoliths that originate from terrestrial vegetation. Significant quantities of BSi are stored in soils (Conley 2002). With increased erosion from cultivated land one may expect an increased contribution of these amorphous Si particles in rivers, and that further implies that phytoliths might have been a continuous source of Si in cultivated areas for centuries. Their role can have a significant influence on Si transport in aquatic systems where BSi dissolves along the river continuum. Something similar has been observed in the Mississippi River when alkalinity increased as a result of land cultivation (Ittekkot 2003; Raymond and Cole 2003). Phytoliths will probably be more efficiently sequestered in reservoirs than diatom BSi due to their solid structure and higher density.

Hydrological alterations

The question remains why the heavily dammed rivers studied, both eutrophic and oligotrophic ones, also show lower DSi concentrations. DSi patterns in the heavily dammed rivers Luleälven and Daugava follow those in the Danube River, but astonishingly do not reach similarly high winter concentrations as in their neighboring rivers of Kalixälven, Oder and Vistula (Figures 2 and 3). One may argue that the geology of the Daugava River is somewhat different, i.e., more consolidated sedimentary rocks, than in the watersheds of the rivers Oder and Vistula, though the soil types of the three watersheds are comparable (FAO 2001). In the case of the watersheds of rivers Luleälven and Kalixälven, the geology is the same. An obvious effect of bedrock geology on DSi concentrations of major global rivers is seen in watersheds with basic volcanic bedrock that have generally higher DSi concentrations, but none of the studied European rivers here has substantial amounts of basic volcanic bedrock. Gaillardet et al. (1999), studying 51 major global watersheds, stressed the significance of physical weathering and runoff, but showed no influence of basin relief on silicate weathering. On a more local scale (Baltic Sea), it has been shown that different annual mean DSi concentrations in various watersheds can be attributed to different vegetation cover and various soil types of the watersheds, but as pointed out by Gaillardet et al. (1999) and Humborg et al. (2004) there is no influence of bedrock types. Weathering of silicate minerals can also be described as a function of temperature and highest DSi concentrations are observed in tropical rivers (Meybeck 1981; Gaillardet et al. 1999). The weathering rate of silicate minerals increases by roughly 8% per one degree temperature using a activation energy of 15 kcal mol^{-1} (which is a typical value for water–rock reactions) (Lasaga 1998), thus, the 80% higher winter DSi concentrations in the rivers Oder and Vistula (~250 μM) compared to the Kalixälven (~140 μM) fit in reasonably well these assumptions, since the average temperature of the southeastern watersheds are ca. 8 °C higher than in the subjected boreal/subarctic watersheds (Table 1). However, neither temperature differences, nor differences in physical weathering, runoff and vegetation cover may fully explain the observed significant differences in DSi concentrations and yields within these two types of studied watersheds.

The effect of damming on lowering DSi winter values in the Luleälven can only partly be explained by water storage in the major reservoirs with long residence times that diminish seasonal patterns. The specific runoff of the Luleälven is about 20% higher as compared with that in the Kalixälven, but the DSi yield of the former constitutes about 60% of the yield of the latter, a pattern observed for all regulated rivers in the area (Humborg et al. 2002). Biological uptake in lakes and reservoirs of these river systems can be excluded, since the reactive phosphorus concentrations are near the detection limit (Humborg et al. 2002) and primary productivity in these boreal/subarctic lakes is as low as 5 g C m^{-2} yr^{-1} (Karlsson et al. 2001).

The water discharge of the dam free Kalixälven during winter originates from the groundwater due to temperatures far below freezing point in this boreal/subarctic environment. DSi concentrations in groundwater are much higher than in surface waters, since the water percolates the soils undergoing weathering reactions (Drever 1997). Winter DSi peaks in the Kalixälven become significantly reduced during spring flood, and DSi concentrations, as well as yields in this river get very close to those in the Luleälven (Figure 3a). During spring the influence of surface runoff from snow melt is predominant, and water from this source has similar low DSi concentrations as in snow, ice, as well as precipitation over the area (Granat 1990; Humborg et al. 2002).

Thus, the decreased DSi concentrations and yields in heavily regulated river systems result from perturbed groundwater-surface water interactions. Downstream of major dams, water level fluctuations are often diminished compared to those of unregulated rivers due to the more evened out flow generated by the hydroelectric power stations, and also owing to storage for flood control (Jansson et al. 2000). This means that the riparian zone downstream of major dams is much reduced, and the exchange processes in the hyporheic zone (White 1993), where mixing between groundwater and surface water occurs, are also diminished. It has been shown that continuous saturation and rapid flushing of the sediment due to hyporheic exchange facilitates Si weathering and is responsible for significant Si supply to small streams (Gooseff et al. 2002; Maurice et al. 2002). Although, to our best knowledge, there are not any studies on the significance of this hyporheic exchange on larger scales, it is obvious that damming simply leads to less contact of surface waters with soils and groundwater in the riparian zone, thus decreases weathering fluxes (Humborg et al. 2002), a process spatially distributed over an entire watershed downstream of a dam. In the heavily regulated Luleälven this effect is even more visible, since significant parts of the former river-bed have been converted into huge reservoirs (10–60 km in length) with eroded shorelines as a result of annual water table fluctuations in the reservoirs. Even in the reservoirs the water has no contact with vegetated soils, in contrast to the predam situation where the water was meandering through the river valleys. Thus, the question might not only be how much reservoirs retain, but to what extent the hydrological alterations decrease the diffusive inputs.

A further possible reason for the lower DSi concentrations in heavily regulated rivers could be that consecutive dams and even more fragmented river stretches in between (Dynesius and Nilsson 1994) decrease the flow rate and increase the overall water residence time in both lentic and lotic waters, thus potentially increasing the productivity of extensive rivers stretches. This 'aging' of waters in regulated rivers is well reported (Vörösmarty and Sahagian 2000). The sharp decrease in TSS concentration, as found in our studies also implies that the turbidity of regulated rivers substantially decreased downstream the dams, probably increasing diatom production and BSi sequestration.

Conclusions

It is not an easy task to separate the various processes responsible for the DSi decrease observed in many rivers and it is of vital importance to disentangle the potential causes of sediment trapping *vs.* hydrological alterations. This is especially important for rivers with a high DSi export that have the potential to influence the coastal biogeochemistry of entire regional seas such as the Changjiang River, where the Three Gorges dam has recently been closed. Damming and hydrological alterations lead not only to autochthonous diatom blooms in the very reservoirs, but they are also responsible for effective trapping of BSi, constituting a significant pool in overall riverine Si stock. For these reasons the effect of altering flow regimes and groundwater–surface water interactions has to be investigated in much more detail. Judging from our regional study, the Si load reduction could have been instrumental in lowering the DSi concentrations in the Baltic Sea (Rahm et al. 1995). Most oligotrophic rivers entering the northern basins of Baltic Sea (206 km^3 or 40% of the total river discharge to the Baltic Sea) are dammed (Humborg et al. 2000). Assuming similar Si yield reductions by ca. 50% as observed in the heavily dammed Luleälven, the upper limit for the Si decrease could be in the order of 300,000 tons Si, which corresponds to ca. 37% of the total Si loads to the Baltic Sea. It is more difficult to estimate the Si load reductions in the eutrophic rivers of the southeastern part of the Baltic Sea catchment (305 km^3 or 60% of the total river discharge to the Baltic Sea), since the Daugava River is most probably not representative for all regulated rivers in the area, and particle trapping occurs also in large natural lakes such as the Lake Ladoga in Russia or Lake Vänern in Sweden.

In contrast to other biogenic elements such as C, N and P, we are only beginning to understand what the major environmental variables that control DSi concentrations and yields in watersheds and coastal systems are. Although we clearly need a watershed perspective to evaluate the various processes, major reservoirs and minor reservoirs, which are much more numerous on a global scale (about 40,000; Vörösmarty and Sahagian 2000), can still be regarded as significant players that are instrumental for lowering Si inputs to coastal seas.

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References

Admiraal W., Breugem P., Jacobs D. and Vansteveninck E.D.D. 1990. Fixation of dissolved silicate and sedimentation of biogenic silicate in the lower River Rhine during diatom blooms. Biogeochemistry 9: 175–185.

Almazov V. 1961. Stock rastverennykh veschestv kotorye vynoseatsya rekami USSR v. Chernoe More. Naukovi Zapiski Odes. Biol. St., Kiev 3: 99–107.

Anon. 2001. Studium kompleksowego rozwiazania problemów stopnia i zbiornika Włocławek – Prognoza skutków społeczno-ekonomicznych – Synteza. Światowy Fundusz na Rzecz Przyrody (WWF), pp. 13–14.

Bidle K.D., Manganelli M. and Azam F. 2002. Regulation of oceanic silicon and carbon preservation by temperature control on bacteria. Science 298: 1980–1984.

Canfield D.E. 1993. Organic matter oxidation in marine sediments. In: Wollast R., Mackenzie F.T. and Chou L. (eds), Interactions of C, N, P and S Biogeochemical Cycles and Global Change. Springer, Berlin, Heidelberg, pp. 333–363.

Conley D.J. 1997. Riverine contribution of biogenic silica to the oceanic silica budget. Limnolo. Oceanogr. 42: 774–777.

Conley D.J. 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem. Cycles 16: Art. No. 1121.

Conley D.J., Schelske C.L. and Stoermer E.F. 1993. Modification of the Biogeochemical Cycle of Silica with Eutrophication. Mar. Ecol.-Progr. Ser. 101: 179–192.

Dean W.E. and Gorham E. 1998. Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. Geology 26: 535–538.

DeMaster D.J. 1979. The marine budgets of silica and Si-32. Ph.D. thesis, Yale University.

Drever J.I. 1997. The Geochemistry of Natural Waters. Prentice Hall.

ius M. and Nilsson C. 1994. Fragmentation and flow regulation of river systems in the northern 3rd of the world. Science 266: 753–762.

Egge J.K. and Aksnes D.L. 1992. Silicate as a regulating nutrient in phytoplankton competition. Mar. Ecol. Prog. Ser. 83: 281–289.

Food Agriculture Organization of the United Nations (FAO) 2001. FAOSTAT: FAO Statistical Databases Accessible through the Food and Agriculture Organization of the United Nations. http://apps.fao.org/.

Friedl G., Teodoru C. and Wehrli B. 2004. Is the Iron Gate I reservoir on the Danube River a sink for dissolved silica? Biogeochemistry 68: 21–32.

Gaillardet J., Dupre B., Louvat P. and Allegre C.J. 1999. Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. Chem. Geol. 159: 3–30.

Garnier J., Leporcq B., Sanchez N. and Philippon X. 1999. Biogeochemical mass-balances (C, N, P, Si) in three large reservoirs of the Seine Basin (France). Biogeochemistry 47: 119–146.

Granat L. 1990. Luft och nederbördskemiska stationsnätet inom PMK. Swedish Environmental Protection Agency, Stockholm (in Swedish).

Gooseff M.N., McKnight D.M., Lyons W.B. and Blum A.E. 2002. Weathering reactions and hyporheic exchange controls on stream water chemistry in a glacial meltwater stream in the McMurdo Dry Valleys. Water Res. Res. 38: 1279, doi:10.1029/2001WR000384.

Humborg C., Smedberg S., Blomqvist S., Mörth C.M., Brink J., Rahm L., Danielson Å. and Sohlberg J. 2004. Nutrient variations in subarctic Swedish rivers: Landscape control of land-sea fluxes. Limnol. Oceanogr. 49: 1871–1883.

Humborg C., Blomqvist S., Avsan E., Bergensund Y., Smedberg E., Brink J. and Mörth C.M. 2002. Hydrological alterations with river damming in northern Sweden: Implications for weathering and river biogeochemistry. Global Biogeochem. Cycles 16: 1039, doi: 10.1029/2000GB001369.

Humborg C., Conley D.J., Rahm L., Wulff F., Cociasu A. and Ittekkot V. 2000. Silicon retention in river basins: Far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. Ambio 29: 45–50.

Humborg C., Ittekkot V., Cociasu A. and von Bodungen B. 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386: 385–388.

Ittekkot V. 2003. A new story from the ol' man river. Science 301: 56–58.

Jansson R., Nilsson C., Dynesius M. and Andersson E. 2000. Effects of river regulation on river-margin vegetation: A comparison of eight boreal rivers. Ecol. Applicat. 10: 203–224.

Karlsson J., Jonsson A. and Jansson M. 2001. Bacterioplankton production in lakes along an altitude gradient in the subarctic north of Sweden. Microbial Ecol. 42: 372–382.

Koroleff F. 1983. Determination of silicon. In: Grasshoff K., Ehrhardt M. and Kremling K. (eds), Methods of Seawater Analyses. Verlag Chemie, Weinheim, pp. 174–183.

Lasaga A. 1998. Kinetic Theory in the Earth Science. Princeton University Press.

Li M. and Cheng H.Q. 2001. Changes of dissolved silicate flux from the Changjiang River into sea and its influence over the last 50 years. Chin. Environ. Sci. 21(3): 193–197. (in Chinese with English abstract).

Maurice P.A., McKnight D.M., Leff L., Fulghum J.E. and Gooseff M.N. 2002. Direct observations of aluminosilicate weathering in the hyporheic zone of an Antarctic Dry Valley stream. Geochim. Cosmochim. Acta 66: 1335–1347.

Meybeck M. 1981. Pathways of nutrients and organic matter from land to ocean through rivers. In: Martin J.-M., Burton J.D. and Eisma D. (eds), River Inputs to Ocean Systems. UNEP, IOC, SCOR, United Nations, New York, pp. 18–30.

Milliman J.D., Rutkowski C. and Meybeck M. 1995. River Discharge to the Sea – A Global River Index (GLORI). LOICZ Reports and Studies.

Panin N. and Jipa D. 2002. Danube River sediment input and its interaction with the northwestern Black Sea. Estuar. Coast. Shelf Sci. 54: 551–562.

Raducu M.C. 2002. Transfer des nutriments dans le basin du Danube et apports a la Mer Noire: Modelisation et bilans. Ph.D. thesis, University of Paris 6.

Ragueneau O., Lancelot C., Egorov V.., Vervlimmeren J., Cociasu A., Deliat G., Krastev A., Daoud N., Rousseau V., Popovitchev V., Brion N., Popa L. and Cauwet G. 2002. Biogeochemical transformations of inorganic nutrients in the mixing zone between the Danube River and the north-western Black Sea. Estuar. Coast. Shelf Sci. 54: 321–336.

Rahm, Sandén P., Wulff F., Stålnacke P. and Conley D.J. 1995. A time series analysis of nutrient inputs to the Baltic Sea and changing DSi/N ratios. Mar. Ecol. Prog. Ser. 130: 221–228.

Raymond P.A. and Cole J.J. 2003. Increase in the export of alkalinity from North America's largest river. Science 301: 88–91.

Reschke S., Ittekkot V. and Panin N. 2002. The nature of organic matter in the Danube River particles and north-western Black Sea seiments. Estuar. Coast. Shelf Sci. 54: 563–574.

Reschke S. 1999. Biogeochemische Variabilitäten in der Schwebstofffracht der Donau und deren Einfluss auf das Sedimentationsgeschehen im nordwestlichen Schwarzen Meer. Ph.D. thesis, Hamburg University.

Turner R.E. and Rabalais N.N. 2003. Linking landscape and water quality in the Mississippi river basin for 200 years. BioScience 53: 563–572.

van Bennekom A.J. and Salomons W. 1981. Pathways of nutrients and organic matter from land to ocean through rivers. In: Martin J.-M., Burton J.D. and Eisma D. (eds), River Inputs to Ocean Systems. UNEP, IOC, SCOR, United Nations, New York, pp. 33–51.

Vörösmarty C.J. and Sahagian D. 2000. Anthropogenic disturbance of the terrestrial water cycle. BioScience 50: 753–765.

White D.S. 1993. Perspectives on defining and delineating hyporheic zones. J. North Am. Benthol. Soc. 12: 61–69.