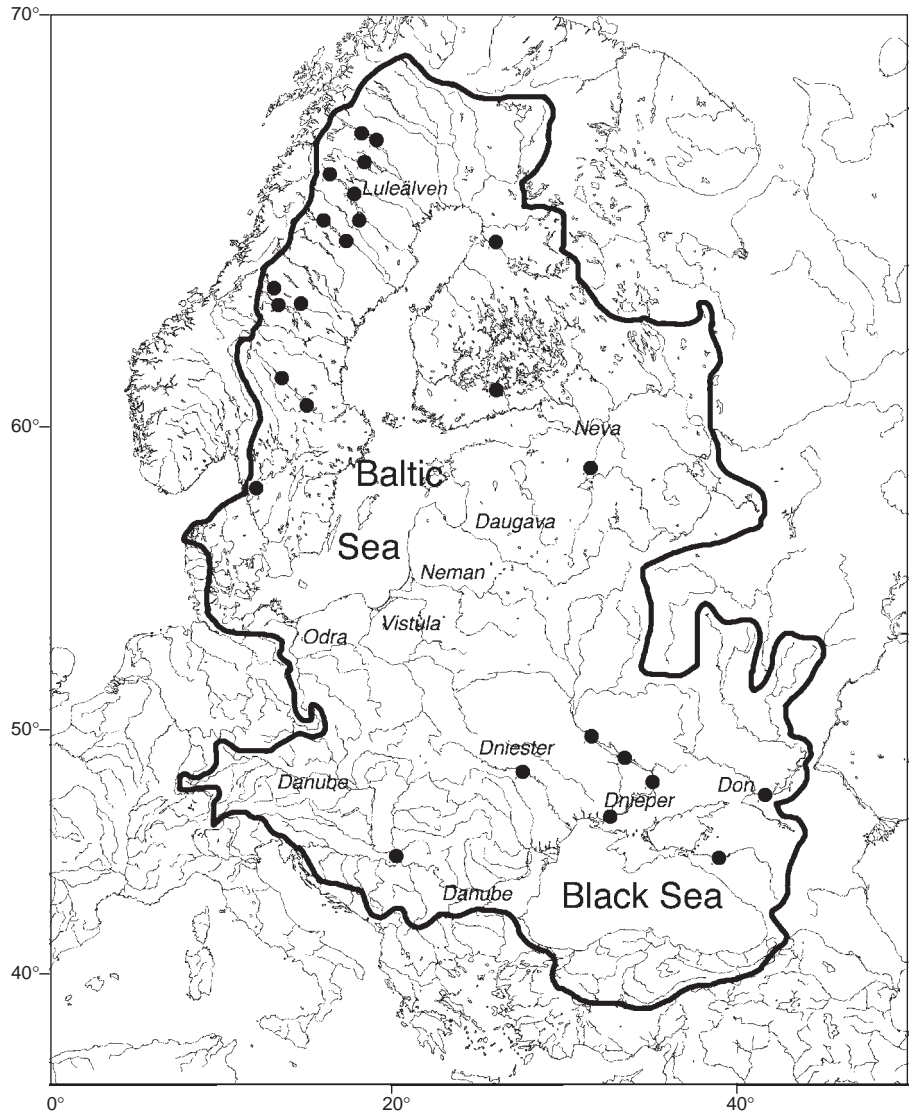


# Silicon Retention in River Basins: Far-reaching Effects on Biogeochemistry and Aquatic Food Webs in Coastal Marine Environments

Regulation of rivers by damming as well as eutrophication in river basins has substantially reduced dissolved silicon (DSi) loads to the Black Sea and the Baltic Sea. Whereas removal of N and P in lakes and reservoirs can be compensated for by anthropogenic inputs in the drainage basins, no such compensation occurs for DSi. The resulting changes in the nutrient composition (DSi:N:P ratio) of river discharges seem to be responsible for dramatic shifts in phytoplankton species composition in the Black Sea. In the Baltic Sea, DSi concentrations and the DSi:N ratio have been decreasing since the end of the 1960s, and there are indications that the proportion of diatoms in the spring bloom has decreased while flagellates have increased. The effects on coastal biogeochemical cycles and food web structure observed in the Black Sea and the Baltic Sea may be far reaching, because it appears that the reductions in DSi delivery by rivers are probably occurring worldwide with the ever increasing construction of dams for flow regulation.

**Figure 1.** Main rivers and location of large reservoirs (max. capacity > 0.5 km<sup>3</sup>) in the Baltic Sea and the Black Sea drainage area.



## INTRODUCTION

The loads of nitrogen (N) and phosphorus (P) discharged to the coastal zone have on a global scale increased by factors 2.5 and 2.0, respectively (1); resulting from human activities such as the synthesis of fertilizer nitrogen and the mining of phosphate rock (2). By contrast, decreasing trends are being observed in the load of dissolved silicon (DSi) (3, 4). These dramatic changes in nutrient loads and composition (DSi:N:P ratios) entering coastal seas will have far reaching effects on coastal ecosystems.

Phytoplankton play a crucial role in marine ecosystems as they represent the base of the marine food web as primary producers. The availability of nutrients is essential for phytoplankton growth and the mixture of nutrients can greatly influence species composition of the phytoplankton community. Diatoms are the most important group of planktonic algae in terms of biomass in the majority of marine ecosystems accounting for 60% of the world's primary production (5). Beside N and P, DSi is also an essential nutrient to diatoms. Diatoms take up DSi and deposit

it in an amorphous form known as biogenic silica (BSi) to construct their cell walls (frustules). If concentrations of DSi are low or depleted, there should be fewer diatoms, allowing other phytoplankton species to bloom in their place (6).

Until recently, there has been only speculation about the potential effects of decreased DSi inputs from land for coastal ecosystems (3, 7). Harmful and nuisance phytoplankton blooms observed worldwide have been attributed mainly to marine eutrophication due to increased N and P inputs (2). In this paper, we will argue that the DSi fluxes are, to a large extent, already altered in rivers. Potential driving forces are eutrophication and damming, both factors enhancing the sedimentation and, thus, retention of BSi and particles containing silicon in the river catchments.

## DATA SETS

The data presented in this paper were derived from different monitoring programs along the Baltic Sea and Black Sea shore-

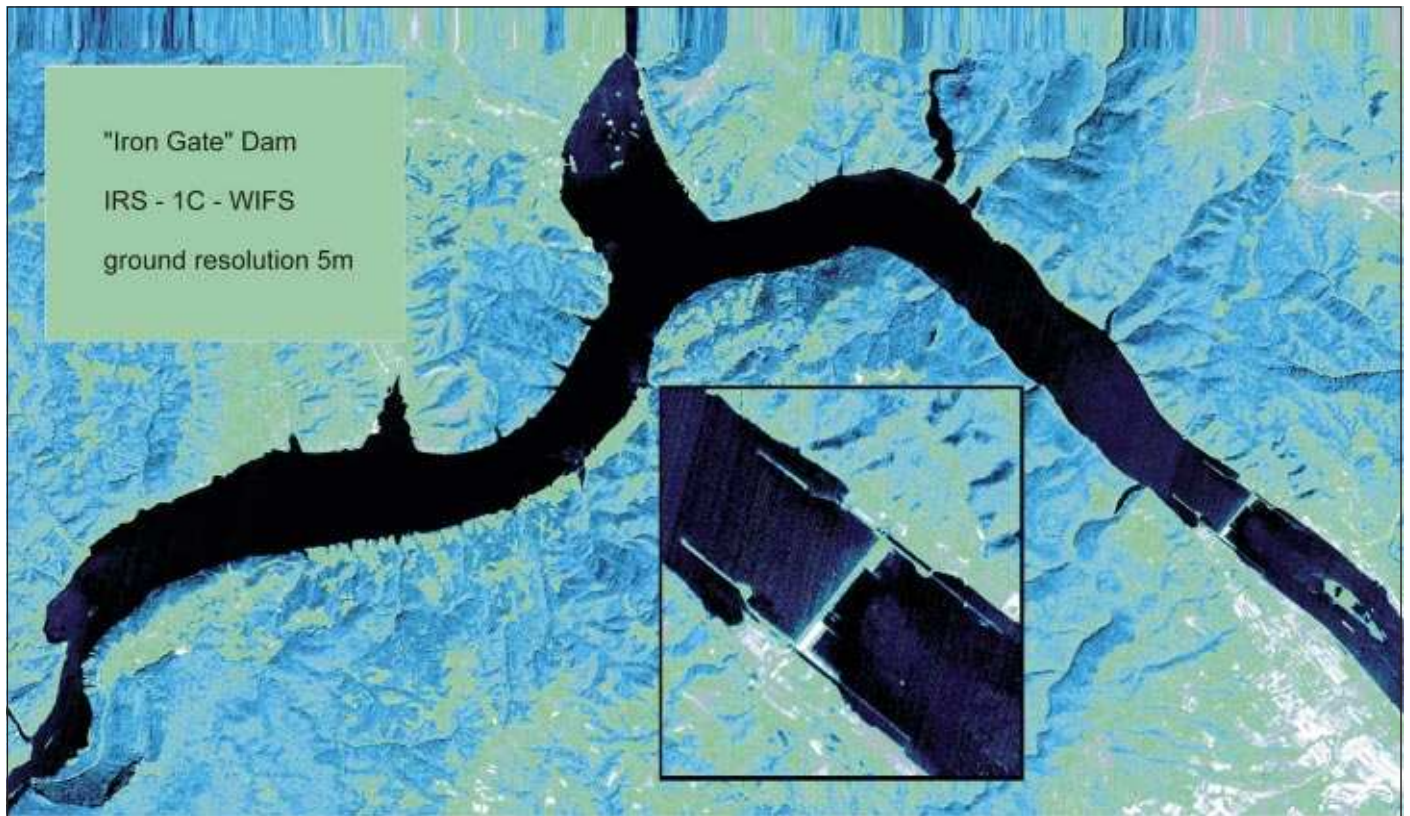


Figure 2. Satellite picture of the "Iron Gate" dam, located at the Yugoslavian/Romanian border (IRS—1C—WIFS, ground resolution 5 m). Courtesy of H. Siegel.

lines, and at the river mouths of major rivers. Many of the major rivers in the catchments of the Baltic Sea and the Black Sea drainage basins are dammed (Fig. 1).

An international monitoring program, performed by all riparian countries, since the 1970s as well as time series data from all rivers allows for an estimate of changes in ecological conditions in the Baltic Sea due to changes in river catchments (8, 9). Data sets that include measurements of nutrients and phytoplankton before and after a dam's construction exist for the Black Sea. A monitoring program is being carried out since the 1960s on the northwestern Black Sea shelf, where the Danube River discharges (10). The Danube dominates the total river discharge into the Black Sea by more than 60%, and changes in the Danube can be more easily traced back to the sea than discharges in the Baltic Sea, with many rivers of similar discharges (11).

Dissolved silicon compounds were determined after standard colorimetric methods (12).

## RESULTS

### Black Sea

The Danube was dammed in the early 1970s at the Serbian/Romanian border where the Danube passes the so-called "Iron Gate" (Fig. 2). Historical measurements of nutrient concentrations from the late 1950s (10), before dam construction, reveals that the DSi concentration was ca. 140  $\mu\text{M}$ , i.e. close to the world average of 150  $\mu\text{M}$  (5). Today, after building of the dam, the mean concentration is only about 58  $\mu\text{M}$  (4). On a yearly basis, the DSi load has been reduced by about 600 000 tonnes. Correspondingly, there has been a decrease in DSi concentrations in Romanian coastal waters. A time series station near the mouth of the Danube reveals that DSi concentration in winter, when primary productivity is negligible, decreased by about 60%, similar to the river concentration (Fig. 3a). The sharp decrease in DSi concentration in the early 1970s corresponds to the onset of dam operation. In contrast, the salinity did not

change at this coastal station indicating that the Danube's freshwater discharges remained uninfluenced. Thus, both time intervals before and after damming are comparable with respect to the hydrological regime. For dissolved inorganic nitrogen and phosphorus compounds no decrease has been observed, because more N and P are emitted by man, compensating the reservoir

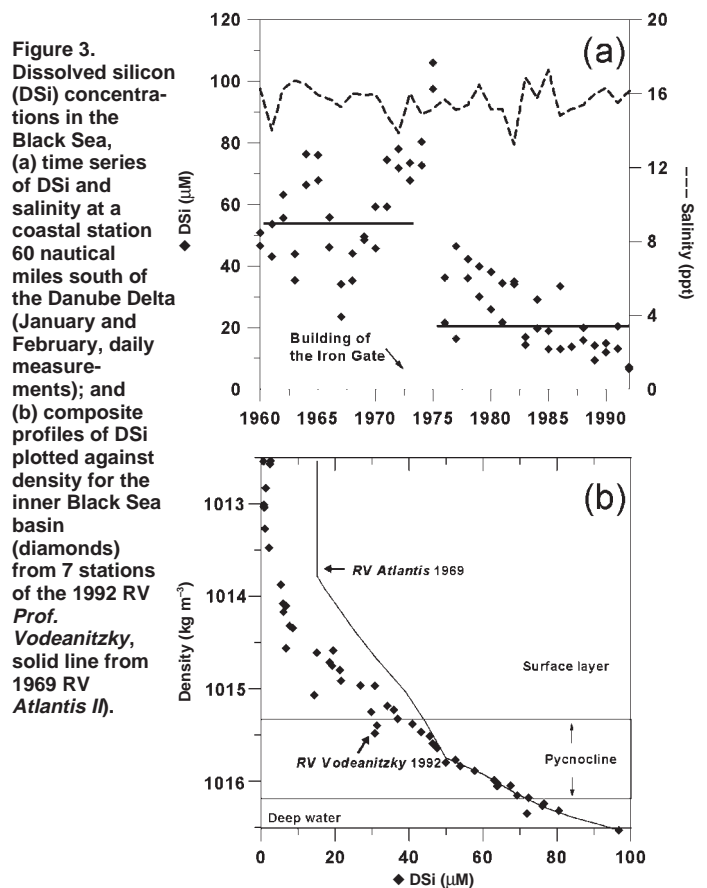


Figure 3. Dissolved silicon (DSi) concentrations in the Black Sea, (a) time series of DSi and salinity at a coastal station 60 nautical miles south of the Danube Delta (January and February, daily measurements); and (b) composite profiles of DSi plotted against density for the inner Black Sea basin (diamonds) from 7 stations of the 1992 RV Prof. Vodeanitzky, solid line from 1969 RV Atlantis II).

uptake. Thus, for the Danube nutrient discharges dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) have been increasing within the last 20 years, whereas DSI decreased dramatically (10).

In the Romanian coastal waters, diatoms (Fig. 4a) have been the most important phytoplankton group before the damming of the Danube River. The altered nutrient discharge patterns of the Danube caused an increase in algal blooms, in addition to the increased biomass a dramatic change in phytoplankton species composition was observed (13). A comparison between periods preceding and following the dam construction (Table 1) clearly reveals that phytoplankton species are not dependent on DSI such as dinoflagellates (Fig. 4b) and that prymnesiophytes became more and more important. While diatom blooms increased by a factor of 2.5, blooms of non-diatoms such as dinoflagellates, the prymnesiophytes *Emiliania huxleyi* (coccolithophore, Fig. 4c) and the facultative toxic species *Chromulina* sp. as well as the Euglenophyte *Eutreptia lanowii* increased by a factor of 6. Before the construction of the dams, blooms of coccolithophores were only reported from far offshore regions, and later in the season (14). The impact of the "Iron Gate" dams on phytoplankton assemblages in the Black Sea can be demonstrated by the following calculations: The annual increase in DIN load of the Danube since the early 1970s is estimated to be about 500 000 t. Assuming a molar DSI:N ratio of 0.65 for *Skeletonema costatum* (15), the predominant diatom species in the area, a DSI uptake of about 650 000 t would be required to remove this nitrogen. Remarkably, this corresponds to the amount of DSI, which is being retained in the reservoir each year (about 600 000 t). This simple calculation implies that a large part of the increase in DIN load of the Danube, after damming of the river, is being removed by non-diatom species. This example also shows that the reduction of DSI by dams can be as important as the increase in N concentrations for the changes in phytoplankton species composition in coastal seas.

It appears that the decreased DSI flux from the Danube has resulted in decreased DSI concentrations in the surface layer throughout the sea. In Figure 3b, DSI concentrations measured during a cruise by US scientists in 1969 (16, 17) are compared with recent data (4). The DSI concentrations decreased drastically in the upper surface layer down to the pycnocline, a sharp density gradient that separates high salinity deep water from a less saline upper surface layer that is influenced by freshwater delivered by the river. The observed decrease amounts to about 1500 mmol m<sup>-2</sup> or 14.7 x 10<sup>6</sup> tonnes for the entire central Black Sea basin. Again, there is a correspondence to the DSI loss due to the Danube dam. Over the last 20 years there has been a retention of DSI of about 11.8 x 10<sup>6</sup> tonnes by the "Iron Gates". Therefore, 80% of the DSI decrease can be related to this dam. Similar effects by dams on DSI discharge of the rivers are conceivable also for the Dnepr and Dnestr (Fig. 1), which contribute about 20% of the freshwater input into the Black Sea. These results show that by far the largest part of the DSI reduction in the central basin is caused by dam construction around the Black Sea.

### Baltic Sea

Larsson et al. (18) estimate a fourfold and eightfold increase in total nitrogen (TN) and total phosphorus (TP) loads, respectively, since the beginning of this century, with a major increase occurring since the 1950s. Recent trend studies during the last decades (19) have shown that generally DIN, and to a lesser extent DIP, have increased in the entire Baltic Sea. An annual increase of roughly 5% for nitrate and 2–3% for phosphate is estimated for the period 1970–1990 (19). During this period the same trends are not found for the riverborne nutrient load (20), while the atmospheric load has increased monotonously since the 1950s (21). While the loads seem more or less constant during

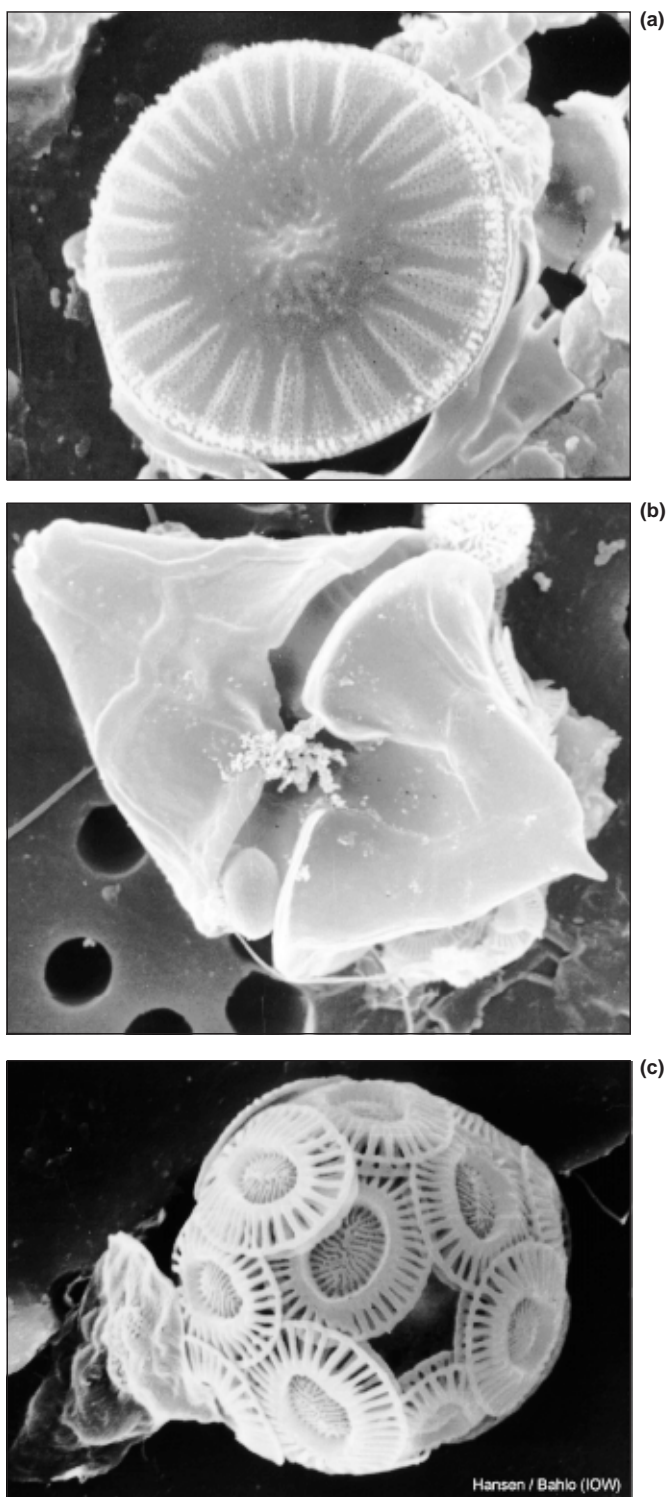


Figure 4. Micrographs showing (a) a diatom *Cyclotella* sp.; (b) a dinoflagellate *Heterocapsa triquetra*; and (c) a prymnesiophyte *Emiliania huxleyi* (coccolithophore) observed in the Danube plume area in 1993.

Table 1. Cell densities and bloom frequency of different phytoplankton groups at different time periods in northwestern Black Sea coastal waters (13), blooms are defined here as > 5 x 10<sup>6</sup> cells L<sup>-1</sup>.

	1960–1970		1986–1990	
	cell densities [10 <sup>6</sup> cells L <sup>-1</sup> ]	number of blooms	cell densities [10 <sup>6</sup> cells L <sup>-1</sup> ]	number of blooms
Diatoms	7–21	8	5–300	19
Dinoflagellates	17–51	4	5–810	14
Euglenophytes	–	–	5–108	6
Prymnesiophytes	–	–	220–1000	3
Total blooms		12		42

this period, the total amounts in the water mass are still increasing, indicating a long time-scale of ecosystem adjustment in the Baltic Sea (8).

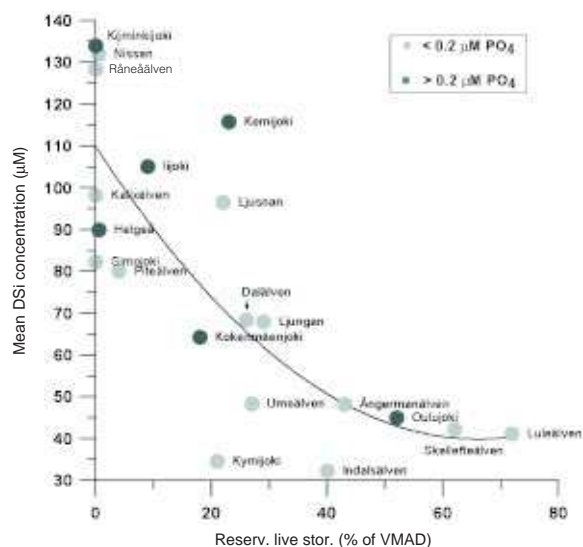
Contrary to DIN and DIP, both the DSi concentration and the DSi:N ratio have been decreasing since the end of the 1960s in the Baltic (22, 23). In fact, the latter ratio is approaching unity, i.e. one that corresponds to the diatom demand. There are no indications, as mentioned above, of a significant change in the DSi load by the rivers during that time. However, major damming operations in the Baltic Sea catchment took place long before the monitoring program started, and occurred mainly in Scandinavia. However, reliable data on nutrient concentrations are difficult to find for that period. In Figure 5, the relation between the river DSi concentrations vs. reservoir live storage of 20 Swedish and Finnish rivers is given. The reservoir live storage is expressed as the percentage of the mean annual discharge of the river system that can be contained in reservoirs (24) and, thus, is a measure for the degree of damming of a river. The “live” storage refers to the volume that can be withheld in, and subsequently released from, the reservoir. An inverse relationship is apparent between the degree of damming and the DSi concentration. Most of these rivers that have been dammed drain into the Gulf of Bothnia. The damming effect can be seen in both more eutrophied as well as in very oligotrophic rivers, which are arbitrarily defined here by their mean phosphate concentration (Fig. 5). The Luleälven, for example, which is the heaviest dammed river in Eurasia, with 72% recorded live storage (24), is a very oligotrophic river with a mean DSi concentration of 41  $\mu\text{M}$ . By comparison, the oligotrophic rivers Råneåälven and Kalixälven, which are not dammed and are situated near the Luleälven, have mean DSi concentrations of 128 and 98  $\mu\text{M}$ , respectively. The very low DSi concentration in the Luleälven can, therefore, to a large extent, be caused by the damming effect.

Assuming a “pristine” DSi concentration of about 110  $\mu\text{M}$  (Fig. 5) the amount of DSi loads reduced by dam constructions in 7 oligotrophic rivers in Sweden (Dalälven, Ljungan, Indalsälven, Ångermanälven, Umeälven, Luleälven, Skellefteälven) can be estimated. These calculations reveal that about 140 000 t  $\text{yr}^{-1}$  less DSi is transported by these rivers annually. For the more eutrophic Finnish rivers Oulujoki and Kokenmäenjoki a further reduction of 20 000 t  $\text{yr}^{-1}$  can be estimated. These numbers agree surprisingly well with estimates of changes in the rate of DSi depletion in the Bothnian Sea and Bothnian Bay (22, 25, 26) of about  $-4\% \text{ yr}^{-1}$ , which corresponds to about 140 000 t  $\text{yr}^{-1}$ . The falling trend in DSi concentrations is observed in the entire Baltic, but is most pronounced in the Gulf of Bothnia, where almost all discharging rivers are heavily dammed and primary production is generally low (25).

In addition to the damming effect, which may be almost entirely responsible for DSi reductions in the Gulf of Bothnia, there is evidence that DSi is also retained with eutrophication in the river basin. Examples of this are the Neva, which is the largest river discharging into the Baltic Sea, and the Götaälv, both draining some of the largest European lakes (Ladoga in Russia and Vänern in Sweden). Both river/lake systems are dammed (reservoir live storage of 4 and  $> 54$ , respectively, (24), but also eutrophied (27, 28). These rivers have the lowest mean DSi concentrations of all the major Baltic Sea rivers averaging ca. 10  $\mu\text{M}$  (23).

It appears, that much of the observed reduction in DSi storage in the Gulf of Bothnia and the Baltic Proper, which is estimated to be about 280 000 t  $\text{yr}^{-1}$  (25), can be explained by damming of lakes in the catchments of the Scandinavian rivers. It is hypothesized that the major rivers draining into the southern part of the Baltic play a minor role, as these rivers are far less dammed and do not contain major lakes in their catchments compared to the boreal rivers and the Neva.

In most parts of the open Baltic Proper, coherent effects of



**Figure 5. River dissolved silicon (DSi) concentrations vs. reservoir live storage (see text) of 20 Swedish/Finnish rivers.**

altered nutrient inputs on the plankton community can not be demonstrated. The lack of measurable effects on the ecosystem structure in the Baltic Sea is probably caused by the limited data set, which starts from 1979, long after perturbations began. However, during the last assessment period (1989–1993) in the HELCOM analysis (29) of the Baltic Proper, it is reported that the proportion of diatoms in the spring bloom has decreased while flagellates have increased. Up to now this was only attributed to mild winters (30).

## DISCUSSION

### Damming and Eutrophication of Rivers

What are the main processes governing the silicon cycle in the drainage areas? The main source of DSi to the coastal ocean is from continental weathering (5, 31). The upper limits of DSi concentrations of natural waters are related to equilibrium reactions between water and various silicon phases and can not be easily determined. DSi concentrations vary in relation to environmental factors such as rock type, relief, vegetation, and water residence times in the soil and river bed (32). In addition, the average temperature of the drainage basin determines the DSi concentration (33). The mean global DSi concentration is about 150  $\mu\text{M}$  (5), which conforms with the one undammed “endmember” of the Scandinavian rivers in Figure 5 as well as with our estimates of the “pre-dammed” Danube concentrations.

It is obvious from the data presented that reservoirs act as a silicon trap, but it is not fully clear what the main processes responsible for the reservoir retention are. It appears that the “artificial lake effect” (34) is present in all sizes of rivers ranging from small Swedish rivers up to major world rivers such as the Danube, the Colorado River (35), or the Fly River (36). The most pronounced example might be the Nile River, where the DSi concentration dropped up to 200  $\mu\text{M}$  after the Aswan High Dam was in operation (37).

Dams convert a river into a lake, increasing water residence times and often improving light conditions in the water column, giving the preconditions for algal growth, including diatoms. High sedimentation rates of diatoms in the reservoir might prevent the return of DSi in the frustule to the water column. On the other hand, there is also a substantial sedimentation of inorganic particles occurring in reservoirs. Large fractions of these clay minerals are silicate minerals. The deposition and loss of

suspended clay sediments from the river system could allow for additional retention of reactive forms of silicon in these artificial deposition sites.

Eutrophication effects in rivers are likely to play a less important role, although diatoms are an important component of phytoplankton composition in rivers (38). Primary production in rivers is often light-limited due to high turbidity and, furthermore, the retention of DSi is limited to available deposition sites. Natural deposition sites are, of course, lakes where eutrophication has definitely increased diatom production and enhanced the retention of DSi (39, 40). One of the best known cases of this phenomenon is the Great Lakes (41).

Eutrophication and the increased sediment accumulation of diatom silica occur not only in lakes (41) and behind dams, but also in coastal marine environments (42). While some of the most significant perturbations of diatom assemblages in the Baltic, as recorded in the sediment record, occurred ca. 1850 (43), significant increases in diatom abundance have been noted in surficial sediments from the northern Baltic Proper (44, 45). It is therefore likely that reductions in the storage of DSi reported in the Baltic (25), can also be influenced by enhanced deposition and storage in Baltic sediments.

### Biogeochemical and Food Web Effects

The importance of DSi in structuring phytoplankton communities has been well-established (6, 46). The resultant effects of DSi depletion on biogeochemical element cycles and food-web structure, however, are poorly known but potentially devastating. Until now, we can only speculate about what a change in diet means for zooplankton and the upper trophic levels including fish. A classical food chain in the coastal sea is dominated by diatoms, which are the usual food for zooplankton (copepods) and contribute in a direct way to large fishable populations in the coastal zone. There is some evidence that the share of coastal diatom production and copepod abundance was lowered due to reduced DSi river discharges (7, 47). Thus, a changing phytoplankton species composition will have repercussions on the entire pelagic food web and might have enormous economic impacts.

The occurrence of potential toxic flagellate blooms has become more frequent in many coastal areas all over the world (46). A similar increase of non-siliceous phytoplankton species as that described for the northwestern Black Sea waters has also been observed in the North Sea (48) or the Mississippi River shelf system (47, 49). There is evidence that an increased DSi retention in the Mississippi and Rhine catchments play an important role for new coastal blooms (47, 50). However, noxious blooms, for example, of *Phaeocystis pouchetii* in the North Sea and the toxic bloom of *Chrysochromulina polylepis* which caused massive fish kills in the Skagerrak in 1988, occurred partially due to changes in the DSi:N ratios caused by marine eutrophication (51). The Black Sea and Baltic Sea examples demonstrate unambiguously that increased DSi retention does not appear only in the receiving waters, i.e. the coastal seas, there is a main contribution taking place in the river basins. Until now, there have been few examples reported of river regulation and/or river eutrophication affecting a marine ecosystem in this way. But this is simply due to the fact that there are only a few data sets available that include measurements of DSi before and after changes in river- and land-use practices far inland. As demonstrated, comparing the DSi concentration at the river mouths with fragmentation and flow-regulation patterns in the catchment can partly solve this problem.

Silicon is also of interest because of its link to the carbon cycle. DSi plays a crucial role in the biological uptake of carbon dioxide by the ocean, by the so called biological pump (52). Globally, diatoms and coccolithophores (calcareous species) are the major players in this process. The efficiency of the biological

pump in the short term is determined by the relative abundance of the two species: diatoms appear to be more efficient in carbon sequestration than coccolithophores. In the open ocean, DSi demand of diatoms is met by DSi-rich water reaching the sea surface by upwelling. In the coastal waters, diatom populations are additionally sustained by DSi input by rivers. A direct relationship between freshwater injection during the monsoon season and an increased flux of carbon and BSi to the deep ocean was shown for the receiving waters of the Ganges/Bramaputra (53). Any changes in the river nutrient mix resulting from DSi reduction can thus have significant impact on carbon cycling in the coastal marine region.

### Outlook

The retention of DSi in aquatic ecosystems has increased worldwide and merits further investigation on land as well as in the sea. We have to know what controls the biogeochemical cycle of silicon in different aquatic systems along the aquatic continuum including natural lakes, reservoirs, rivers, and the coastal seas up to the open ocean. Little is known about changes in the production of DSi with land use. The long-term effects of disturbance with agriculture or the more recent effect of acid rain on weathering, and thus the production of DSi, is not known. The obviously significant physicochemical vs. biological DSi retention in reservoirs and lakes has to be further investigated.

Today, about 36 000 dams are in operation (54), 20% of the global river flow is dammed or diverted (55). The possible ecological effect in the sea might have important implications for SE Asia, where fertilizer use is rapidly increasing (2) and major rivers are being dammed at alarming rates. The Three Gorges damming of the Yangtze River is one of the latest impressive examples. On the Yellow River low rainfall and the construction of dams have led to a nearly 50% drop in water and sediment discharge (56). However, societal benefits of dams and reservoirs are obvious, and include the modulation of river flow between wet and dry periods, irrigation for agriculture and the production of hydroelectric power. Therefore, it might not be the question of whether a dam is built, but how a new dam can be built to minimize undesirable side effects (56).

Our hypotheses on the potential effects on biogeochemical cycles in the coastal seas are admittedly speculative and we are aware that it is a big jump from the results presented for the Baltic Sea and the Black Sea to tropical oceans. However, coastal waters account for about 30–50% of global oceanic “new” production (57). It is hardly possible to overestimate the potential effects on the marine food web: reducing the diatom-to-zooplankton-to-higher trophic level food webs, and increasing the proportion of flagellate algae (7, 47). More harmful algal blooms, less fish, and changes in carbon sequestration might be additional possible effects.

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