Hydrological Alterations and Marine Biogeochemistry: A Silicate Issue?

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Freshwater and sediment inputs from rivers play a major role in sustaining estuarine and coastal ecosystems. Nutrients from rivers promote biological productivity in estuaries and coastal waters, and the sediments supplied by the rivers stabilize deltas and coastal zones and help to maintain ecosystems along the periphery of landmasses. In the last few decades, human activities have caused enormous changes both in the nature and quantity of these inputs. Fluxes to the oceans of mineral nutrients, such as phosphate and nitrate, have increased worldwide by more than a factor of two (Meybeck 1998). This increase has led to accelerated algal growth, known as eutrophication, and consequently to deterioration in water quality because of oxygen depletion. Toxic algal blooms occurring in coastal waters, which have devastating effects on fisheries and on biodiversity in general, are also attributable to eutrophication. Oxygen-deficient conditions, in turn, promote the production of greenhouse gases such as nitrous oxide and methane and their emission from coastal waters to the atmosphere.

Most studies addressing the causes of eutrophication have concentrated on the elements nitrogen and phosphorus, mainly because both nutrients are discharged by human activities. Silicate, however, also plays a crucial role in algal growth and species composition. For example, the growth rates of diatoms (silica-shelled phytoplankton) are determined by the supply of silicate. Researchers have noted a decrease in the level of dissolved silicate in many coastal marine regions of the world in the last few years (Conley et al. 1993). The increased growth of silicate-utilizing diatoms—the result of nitrate- and phosphate-induced eutrophication—and the subsequent removal of fixed biogenic silica via sedimentation out of the water column (Billen et al. 1991, Rahm et al. 1996) are thought to explain the decrease in dissolved silicate. The resulting changes in the ratios of nutrient elements (e.g., silicon:nitrogen:phosphorus, or Si:N:P) have caused shifts in phytoplankton populations in water bodies (Admiral et al. 1990, Turner and Rabalais 1994). Shifts from diatoms to nonsiliceous phytoplankton have been observed much earlier in the season in several estuarine and coastal regions (in the receiving marine waters of the Rhine river, for example).

The source, transport, and sink characteristics of silicate, as they relate to changes in the hydrology of rivers, are distinct from those of nitrogen and phosphorus. Large-scale hydrological alterations on land, such as river damming and river diversion, could cause reductions of silicate inputs to the sea (Humborg et al. 1997). By contrast, although all nutrients (nitrogen, phosphorus, and silicon) get trapped in reservoirs behind dams, nitrate and phosphate discharged from human activities downstream of the dams more than make up for what is trapped in reservoirs; for silicate, there is no such compensation. The resulting alteration in the nutrient mix reaching the sea could also exacerbate the effect of eutrophication—that is, silicate limitation in perturbed water bodies can set in much more rapidly than under pristine conditions, leading to changes in the composition of phytoplankton in coastal waters.

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In this article, we examine the available information on the potential long-term impact of hydrological alterations on the biogeochemistry of marine systems. We specifically examine the effect of modification of silicate inputs from rivers as a result of upstream damming.

The carbon–silica link
Cycles of silicon and carbon have been intimately linked through geological time. Silicate minerals (clay minerals), because of their surface charge and repeating crystal structure, are implicated in the concentration of simple organic molecules and formation of complex ones early in the development of life on earth (Cairns-Smith 1985). Through the process commonly known as biomineralization (biologically mediated mineral formation), the organic carbon compounds that organisms synthesize, such as proteins and carbohydrates, mediate the formation of silicon-containing minerals (biogenic silica-opal) in frustules of diatoms and radiolarians (Hecky et al. 1973, Degens 1976). Weathering of silicate rocks on land is considered to be a sink for atmospheric carbon dioxide (CO₂), albeit on long time scales (Berner et al. 1983, Wollast and Mackenzie 1986, Brady and Carrol 1994). Although the rate of CO₂ consumption by weathering reactions is much slower than its rate of cycling through organisms, weathering processes may be important in controlling the long-term concentrations of CO₂ and oxygen (O₂) in the atmosphere and in the ocean. Chemical weathering of silicates on land is also the process that supplies dissolved and particulate silicate to rivers and ultimately to oceans. More than 80% of the total input of silicate to the oceans is supplied by rivers (Treguer et al. 1995).

Silicate inputs fertilize the seas by stimulating the production of diatoms, which fuel food webs and play a crucial role in the biological uptake of CO₂ by the ocean through operation of the so-called biological pump (Smetacek 1998). The exchange of CO₂ between the atmosphere and the ocean is affected by both physical and biological processes (Figure 1; Heinze et al. 1995). The physical exchange process, known as the solubility pump, is characterized by the dissolution of CO₂ in surface waters and its transfer to the deep sea in sinking water masses (known as the solubility pump); CO₂ is brought back to the atmosphere via upwelling of water masses. Figure modified from SCOR (1990).
ways. An efficient organic carbon pump means a net withdrawal of CO$_2$ from the atmosphere because the formation of organic matter during photosynthesis decreases the total carbon content and partial pressure of CO$_2$ in the surface layers:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$$

Although carbonate production reduces the total dissolved inorganic carbon in the surface layers, the reaction increases the partial pressure of CO$_2$ at the surface ocean, thus driving CO$_2$ from the ocean to the atmosphere. For each mole of carbonate formed, a mole of CO$_2$ is released:

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

Diatoms (silica-secreting organisms) and coccolithophorids (carbonate-secreting organisms) are among the major players in the working of the biological carbon pump (Figure 2). Because of the difference in the ways the two reactions affect the CO$_2$ system in the surface ocean, the efficiency of the biological pump in the short term is determined by the relative abundance of the two species: Diatoms are more efficient than coccolithophorids at carbon sequestration. The efficiency of the biological pump is also reflected in the nature of material settling out of the surface layers of the oceans. In areas where the biological CO$_2$ pump works efficiently to remove CO$_2$, the material settling to the ocean's interior exhibits higher ratios of biogenic silica to carbonate and organic carbon to carbonate carbon ($C_{\text{org}}/C_{\text{carb}}$, also called rain ratios), which are indicative of the efficiency of CO$_2$ sequestration at the sea surface (Berger and Keir 1984).

### River inputs and the marine response

In vast areas of the world's oceans, the silicate demand of diatoms is met by the silicate-rich waters reaching the sea surface by upwelling. In such areas (e.g., the equatorial upwelling zone), dissolved silicate concentrations set the upper limit on the total possible biological utilization of inorganic carbon. Diatoms appear to be responsible for most of the new primary production in these areas (Dugdale and Wierssen 1998).

Diatom populations in coastal waters are also sustained by silicate inputs from rivers. Although coastal seas represent at most 10% of the oceanic area and less than 0.5% of oceanic volume, they make a disproportionately high contribution to global marine primary production (Mantoura et al. 1991). Recent estimates show that the coastal seas contribute 30–50% to the new primary production of global oceans (Pearl 1995). Moreover, deltaic and shelf sediments incorporate approximately 80% of the organic carbon sequestered in modern marine sediments (Berner 1982). Thus, alterations in river inputs and the accompanying potential changes in species composition of diatoms could have a significant impact on marine biogeochemical cycles.

Observations from the northern Bay of Bengal in a year of enhanced freshwater and sediment inputs provide an example of how marine biogeochemical processes respond to changing river inputs (Figure 3). The Bay of Bengal receives sediment and freshwater inputs from some of the largest rivers of the world, including the Ganges, the Brahmaputra, and the peninsular Indian rivers. The inputs exhibit high seasonal variability, with approximately 70–80% of the annual water and sediment discharge occurring during the southwest monsoon (Ittekkot et al. 1985). These rivers also discharge large amounts of dissolved silicate, which accounts for approximately 5% of global river inputs (Daniela Unger and Venugopalan Ittekkot, University of Hamburg, unpublished data). Most of these inputs drain into the bay during the southwest monsoon.

The impact of large quantities of sediments and fresh water entering the Bay of Bengal from the Ganges—
Brahmaputra river system is visible in the nature of particles settling from the sea surface to the seafloor (Ittekkot et al. 1991). Results from sediment traps in the northern Bay of Bengal (NBBT N in Figure 3) showed that the quality and quantity of material reaching the deep sea vary with inputs from the Ganges–Brahmaputra river system (Figure 4a; Ittekkot et al. 1991). Most of the material reaches the deep sea during the 3 months of the southwest monsoon, which is also the period of highest river discharge; qualitative changes are also at a maximum during this period.

Increased river inputs lead to a change in biological community structure, with an increase in the silica-secreting diatoms relative to the carbonate-secreting coccolithophors. These changes are recorded in the material collected in sediment traps, especially in their opal (biogenic silica):carbonate ratios. There is also a concomitant increase in the production rates of organic carbon relative to carbonate carbon during the southwest monsoon.

The sediment traps deployed farther from the river mouths, approximately 200 km south of the first location (NBBT S in Figure 3) yielded revealing results as to the possible role of river inputs. The settling particles are characterized by low fluxes and an absence of pronounced seasonal signals (Figure 4b; Schäfer et al. 1996). Fluxes of biogenic silica are also low and uniform (Figure 4c), indicating lower contribution from diatoms. The difference influxes and their quality at the two sediment trap locations reflect the lateral extent of the river plumes (with NBBT S being away from the plume), with diatom blooms at plume fronts acting as barriers both for dissolved nutrients and for river-derived lithogenic (mineral) material. This material acts as ballast in the formation of rapidly sinking aggregates, which transport the freshly formed biogenic silica from diatom blooms and organic matter to the sea bottom (Figure 5; Ittekkot et al. 1992).

Similar silicate removal associated with diatom blooms has been observed in the Amazon River estuary (Milliman and Boyle 1975), and diatom frustules are the major components detected within brackish water lenses at the mouth of the Amazon (Milliman et al. 1975, Kidd and Sander 1979). The influence of the Amazon River is observed also in the hydrochemistry and biological productivity of the western tropical Atlantic and the eastern Caribbean Sea during spring and summer, which is the
The nature and fluxes of material to the deep sea exhibit variability that appears to be related to the northwestern movement of the plumes of the rivers Amazon and Orinoco (Deuser et al. 1988). Hydrological alterations and river inputs

The most widely discussed and well-documented impacts of large-scale hydrological alterations (river damming and river diversion, for example) on marine systems are reductions in water and sediment discharge (e.g., Milliman et al. 1984, Halim 1991). Coastal erosion and changes in fisheries are some of the immediate effects of these reductions (FAO 1995). It appears, however, that hydrological alterations can introduce more subtle changes in the chemistry of river inputs, with long-term consequences for coastal ecosystems. An example is the Danube River and its impact on the Black Sea.

The Danube, which contributes approximately 70% of river inputs into the Black Sea, was dammed in 1970–1972 approximately 1000 km upstream, on the Yugoslavian–Rumanian border at a place called “Iron Gates.” Comparison of the available data from the pre- and postdam periods suggests significant changes in silicate inputs as a result of water and sediment storage in reservoirs at Iron Gates, with consequent changes in the biogeochemistry of the river, the adjacent coastal waters, and the entire Black Sea basin.

Retention of silicate in the upstream reservoir has led to an overall decrease in silicate concentration from predam levels of 140 µmol/L to postdam levels of 58 µmol/L, with a drop in the annual silicate load from $800 \times 10^3$ tons (Si$_4$O$_4$) to $230–320 \times 10^3$ tons (Humborg et al. 1997). Winter silicate concentrations in coastal waters have decreased from predam values of 55 µmol/L to 20 µmol/L in the postdam period (Figure 6a; Cociasu et al. 1996). In contrast, various human activities have caused dissolved inorganic nitrogen concentrations to decrease from a median predam value of approximately 1.3 µmol/L to a postdam median of 7.9 µmol/L. The result is a change in the nutrient mix available for plankton production because the Si:N ratio decreased from 42 to approximately 2.8.

The timing of these changes correlates well with observed increases since the beginning of the 1970s in phytoplankton bloom frequency, cell densities, and the number of bloom-forming species in the Black Sea (Bodeanu 1993). Diatom blooms increased by a factor of 2.5, whereas blooms of nondiatoms, such as dinoflagellates, the prymnesiophyte Emiliania huxleyi (a coccolithophore), and the facultatively toxic Chromulina species, increased by a factor of 6. Carbonate-secreting coccolithophorids, which were usually reported only from offshore areas of the Black Sea during the predam period, are now found near the Danube plume at low salinities (Humborg et al. 1997).

The silicate decrease is evident even in the surface waters of the central Black Sea. Data show a decline of silicate concentrations from a historical level of approximately 17 µmol/L in 1969 to nearly 0 µmol/L in 1992 (Figure 6b). Model calculations using geochemical proxies, such as barium (Ba) and radium ($^{226}\text{Ra}$), for silicate in the Black Sea appeared to support previous suggestions that enhanced diatom production and the sedimentation of biogenic silica were primarily responsible for the observed decrease in silicate in the central Black Sea (Falkner et al. 1991). However, direct measurements of Ba sedimentation fluxes using sediment traps were lower by a factor of 10 than the flux expected from the model (Hay et al. 1990). Thus, the silicate decrease would appear to be related more to a reduction in inputs from the Danube caused by river damming than to the increased removal of biogenic silica by diatom production.

The estimated reduction in the Danube’s supply of silicate can account for 80% of the observed silicate decrease in the central Black Sea basin (Humborg et al. 1997). If dams have similar effects on silicate discharge in other rivers draining to the Black Sea, the largest part of the silicate reduction in the central Black Sea basin can be attributed to dams. Data from the Nile River support this claim. Dissolved silicate concentrations at the mouth of the Nile dropped by almost 200 µmol/L after the Aswan High Dam began operation (Whaby and Bishara 1980).
Outlook

The observed continuing increase in nutrients such as nitrate and phosphate and the reduction in silicate concentrations in rivers clearly indicate that nonsiliceous phytoplankton species will be more prolific in the receiving waters of many dammed rivers of the world. The occurrence of potential toxic flagellate blooms may become more frequent. Many important regulatory and socioeconomic functions of water bodies will be affected. The ability of these water bodies to sustain economically important fisheries resources will be reduced; severe perturbations can be expected in the biogeochemical cycling of elements, with adverse consequences for the role of coastal seas as sinks for anthropogenic gases such as CO₂.

The effects can be expected to be more severe in enclosed seas, which are already under severe environmental pressure, than in open-ocean systems where silicate inputs from offshore exchange may offset the decrease in river inputs. However, the recently reported link between the pattern of silicate uptake and the availability of iron from river inputs indicates that the effects of changing river inputs may go beyond coastal aquatic systems (Hutchins and Bruland 1998); reduction of river inputs of iron because of hydrological alterations can affect the uptake of silicate in nutrient-rich waters in upwelling regions away from the coast.

One of the issues to be resolved is whether the reduction in silicate in coastal waters is caused by its increased removal through enhanced diatom production or by a decrease in direct inputs from rivers. Although both processes are likely to effect silicate decreases, enough evidence is available to suggest that hydrological alterations such as river damming and river diversions could be the crucial factors (Milliman 1997). Given the large numbers of dams in operation today (Rosenberg et al. 2000) and the extent of river flow that is dammed or diverted (Vörösmarty and Sahagian 2000), reduction of silicate could be of global significance.

Dugdale et al. (1995) and Dugdale and Wilerson (1998) have shown the importance of understanding silicate cycling in open-ocean systems, and much research is under way on this front. However, more water-quality studies of rivers, estuaries, and coastal seas are needed. A better understanding of the silica cycle and its interaction with other life-supporting elements is a prerequisite for assessing the carrying capacity of water bodies and for developing scientifically sound strategies to reduce the risk of environmental degradation of these bodies of water.

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Figure 6. Silicate concentrations in the Black Sea. (a) Mean winter silicate concentrations (solid diamonds) at a coastal station (Constanta, Romania) approximately 60 nautical miles south of the Danube River mouth. The bold lines show overall medians from 1960–1972 and 1973–1992. The salinity at this station has remained at approximately S = 15 (dashed line), indicating that the effect of the Danube on salinity has not changed over time. (b) Composite profiles of silicate plotted against density; observations for 1969 (solid line) from RV Atlantis and observations for 1992 (diamonds) from RV Vodeanitzky (diamonds; figure after Humborg et al. 1997).