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# Responses of Coastal Ecosystems to Anthropogenic Perturbations of Silicon Cycling

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Changes in phytoplankton dynamics and food webs have been observed in many coastal ecosystems and are related to long-term decreases in riverine Si:N and Si:P nutrient ratios (reviews in Smayda 1990; Conley et al. 1993; Turner et al. 1998). The most obvious explanation for the observed decrease of Si:P and Si:N ratios is eutrophication. Urbanization and agricultural and industrial activities have led to large increases in the delivery of N and P along the land–ocean continuum. On a global basis, the fluxes of these elements to the oceans have increased by a factor of two; it has long been thought that at the same time, DSi fluxes have remained constant because the major source of DSi to rivers is natural silicate rock weathering (Chapter 2, this volume). Numerous reviews have described excessive inputs of N and P compounds to coastal waters (e.g., Nixon et al. 1996; Howarth et al. 1996), their effects on coastal waters (e.g., Cloern 2001), and the subsequent nutrient management strategies needed for sustainable use of coastal zones (Conley 2000). However, Si:N and Si:P ratios also decrease after an anthropogenic reduction of DSi concentrations along the aquatic continuum from land to ocean.

### Silica Depletion in Aquatic Systems

Three major mechanisms can contribute to the proposed silica depletion. Two are well known (eutrophication and hydrologic management), and the third one (increasing biodeposition by invasive species) remains to be explored (Ragueneau et al. 2005).

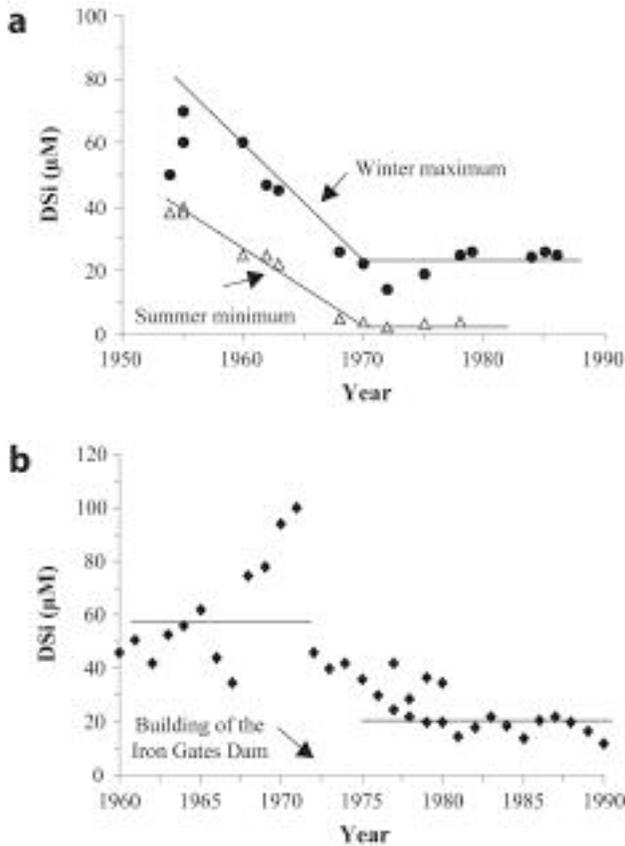
Increased N and P loading—eutrophication—increases aquatic primary production and, in many systems, diatom production. Subsequent increases in the sedimentation

rate of diatoms can lead to increasing amounts of diatoms and BSi stored in the sediments, eventually leading to a reduction in DSi supplies to the water column, especially in systems with long residence times (Conley et al. 1993). This nutrient-driven alteration of the biogeochemical Si cycle was first described for the North American Great Lakes (Schelske et al. 1983), but it has also been observed in small lakes (Engstrom et al. 1985; Schelske et al. 1987) and is relevant for the coastal zone, with a number of coastal margin systems showing declines in DSi concentrations that are related to anthropogenically induced eutrophication (review in Conley et al. 1993).

Strong reduction in DSi concentrations in rivers has also been observed after dam construction (the so-called artificial lake effect; Van Bennekom and Salomons 1981), as in the Nile River (Wahbi and Bishara 1979) and the Mississippi River (Turner and Rabalais 1991). Humborg et al. (1997) observed a direct link between dam building, nutrient ratio, and coastal ecosystem structure in the Danube–Black Sea system. In these systems, DSi reductions have been assumed to occur with increased diatom growth after increased residence time of waters in the reservoirs and subsequent retention of Si as diatoms are buried in accumulating sediments behind dams (Figure 12.1). Two other mechanisms to account for DSi reduction with damming are the trapping of phytoliths or other forms of amorphous silica during sedimentation behind dams, removing an important component of particulate Si carried by rivers (Conley 2002), and changes in vegetation associated with hydraulic manipulations that affect the weathering fluxes of DSi, thereby leading to the observed DSi reduction (Humborg et al. 2002). Both mechanisms are discussed in more detail in Chapters 3 and 5.

Another influence on the Si cycle along the land–ocean continuum is increased biodeposition. Indeed, suspension feeders filter enormous amounts of water (Budd et al. 2001); they consume diatoms and produce large quantities of biodeposits enriched in Si relative to C or N because they have no known metabolic need for Si (Ragueneau et al. 2005; see also Tande and Slagstad 1985 or Cowie and Hedges 1996 for an analogy with pelagic grazers). The effects of biodeposition on the Si cycle and ecosystem functioning have been suggested (Chauvaud et al. 2000) and observed at a seasonal scale in terms of phytoplankton dynamics (Ragueneau et al. 2002a; Chapter 11, this volume).

More recently, Ragueneau et al. (2005) explored the consequences of such a mechanism for the Si cycle on longer time scales. Budget calculations demonstrate that in the Bay of Brest, annual Si biodeposition represents nearly 80 percent of DSi river inputs. Some 70 percent of the BSi biodeposited redissolves (Ragueneau et al. 2002a). However, the biodeposition flux is so important and the preservation conditions in *Crepidula fornicata* mats so good (nearly 30 percent of the BSi annually biodeposited eventually gets preserved; Ragueneau et al. 2005) that the annual Si accumulation amounts to about 20 percent of DSi river inputs. Although this retention efficiency is close to the global mean proposed by DeMaster (1981), it is twice as high as the one used at global scale by Tréguer et al. (1995) and probably much higher than it was before *C. fornicata* invaded the ecosystem. In many ecosystems biodeposition increases year after year with the development



**Figure 12.1.** Illustration of the DSi depletion hypothesis. (a) Decreasing DSi concentrations with eutrophication in Lake Michigan (redrawn from Schelske et al. 1983). (b) Declining DSi concentrations at the Danube River mouth after construction of the Iron Gates dam in the early 1970s (redrawn from Humborg et al. 1997).

of aquaculture and the accidental proliferation of invasive species (Mack et al. 2000; Ruiz et al. 2000). We hypothesize that increasing biodeposition may constitute another route for silica depletion that does not necessarily involve increased diatom production but simply increased BSi preservation. It will be important to test this hypothesis, first in the Bay of Brest ecosystem and then in the many places where biodeposition is increasing. Possible ways of testing this mechanism include looking at changes in BSi accumulation rates in such ecosystems and looking at monitoring data downstream of invasions to search for changes in DSi concentrations.

## Anthropogenic DSi Inputs

It was recently recognized that there are significant anthropogenic sources of DSi. Soluble silicates such as sodium silicates (water glass) are some of the largest-volume synthetic chemicals in the world and are used in both industrial and household products, such as laundry detergents (van Dokkum et al. 2004). Recent estimates suggest that in Western Europe the additional load of anthropogenic DSi into rivers from industries and households contributes only 2 percent of the annual DSi in Western Europe (van Dokkum et al. 2004). However, locally, and especially during times of low DSi concentrations or near cities, substantial inputs of DSi may affect local mass balances. Additionally, various forms of soluble silicates are being used as commercial fertilizers, especially on crops such as rice and sugarcane, which have high demands for Si (Datnoff et al. 2001). DSi as a fertilizer is also being used in soilless greenhouse systems. The quantities of the additional sources of DSi are poorly constrained at present.

## Ecosystem Response to Decreasing Si:N and Si:P Ratios

### *Switch from Diatoms to Flagellates: The DSi Paradigm*

The growth of diatoms depends on the presence of DSi, whereas the growth of nondiatom phytoplankton does not. Diatoms use DSi, mostly  $\text{Si}(\text{OH})_4$  (Del Amo and Brzezinski 1999), essentially to build their frustules (Guillard and Kilham 1978). This silica wall may protect them against predators (Hamm et al. 2003) or increase their ability to acquire inorganic carbon ( $\text{CO}_2$ ) from seawater (Milligan and Morel 2002). In the 1970s, many experimental studies were devoted to determining DSi uptake parameters (Officer and Ryther 1980 and references therein), namely the maximum uptake rate ( $\mu_{\text{max}}$ ) and the half-saturation constant ( $K_s$ ). They showed that  $K_s$  values ranged between 0.5 and 5.0  $\mu\text{M}$  (i.e., well within the range of DSi concentrations encountered in the field), suggesting that “low silicate concentrations may exert a selective influence on the species composition of phytoplankton populations in the sea” (Paasche 1973). Diatom physiology and DSi kinetic uptake parameters are discussed in more detail by Claquin et al. in Chapter 9.

### First Evidence of DSi Limitation

Interestingly, the first evidence of DSi limitation has been reported in lakes. Pearsall (1932) and then Lund (1950) observed a rapid decline of diatoms with DSi concentrations dropping below 8  $\mu\text{M}$ . Kilham (1971) related the seasonal succession of diatoms in eutrophic lakes to changes in ambient DSi concentrations. In the same period, Schelske and Stoermer (1971) related shifts from diatoms to green and blue-green algae in Lake Michigan to DSi depletion, after increased diatom growth and P inputs.

Officer and Ryther (1980) extended this idea to marine waters by reviewing a few case studies in North American estuaries and coastal waters. A sequence from spring

diatoms to summer flagellates is a common occurrence in temperate coastal waters (Margalef 1958). Officer and Ryther (1980) related it to DSi availability, which becomes limiting after spring uptake by diatoms and lower subsequent dissolution of diatom Si compared with N and P, which are biologically mediated.

### Two Decades of Evidence Sustaining the Paradigm

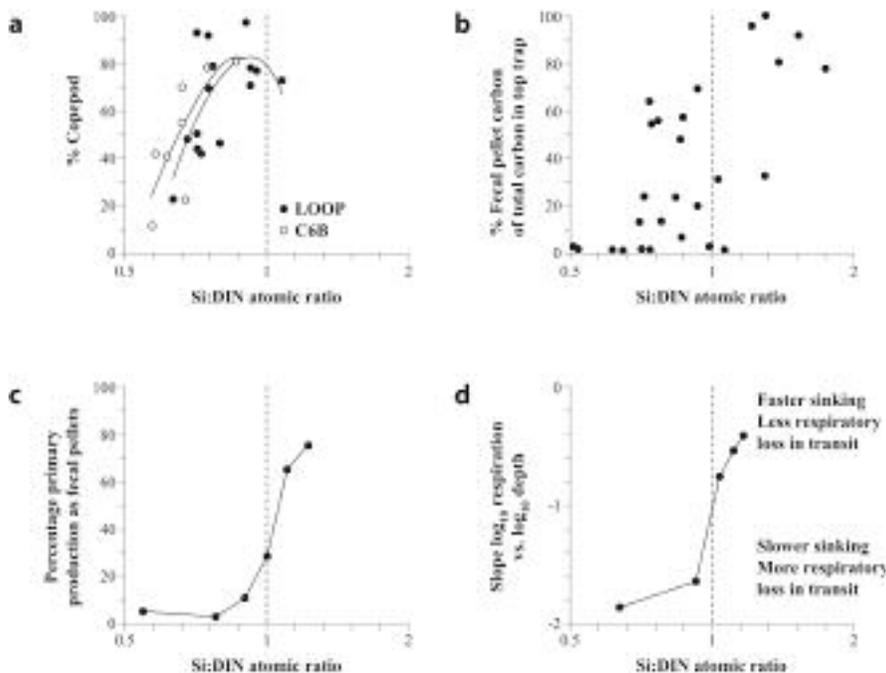
The Si:N and Si:P ratios are declining at the output of many rivers because of increasing N and P loadings, decreasing DSi concentrations, or both. Year after year, coastal waters move from N to Si limitation (Fransz and Verhagen 1985; Conley and Malone 1992; Ragueneau et al. 1994). Ecosystems move from a natural sequence (from a new production regime during spring, dominated by diatoms, to a regenerated production regime during summer, dominated by flagellates) to a perturbed sequence in which the shift occurs earlier in the season and flagellate blooms become much bigger because they occur under a new production regime, making use of the excess N and P that could not be used by diatoms because of DSi limitation (Billen et al. 1991).

This phenomenon is not confined to a few case studies. Smayda (1990) related the increasing frequency and magnitude of harmful algal blooms in many ecosystems (Baltic Sea, Kattegat, Skagerrak, Dutch Wadden Sea, North Sea, Black Sea) to long-term declines in Si:N and Si:P ratios. Justic et al. (1995) presented two more case studies in the Adriatic Sea and the northern Gulf of Mexico. They noted that if “historically, rivers carried DSi well in excess to DIN and DIP [dissolved inorganic nitrogen and phosphorus, respectively], at present, many world rivers are beginning to experience a stoichiometric nutrient balance or even a DSi deficiency.” Perhaps the two best case studies are located on the Louisiana and northwestern Black Sea continental shelves, at the mouths of the Mississippi and Danube rivers, respectively.

Mostly as a result of large increases in N and P fertilizer use, the DSi:DIN ratio has decreased from 3:1 to 1:1 in the twentieth century in Louisiana shelf waters (Turner and Rabalais 1991). Other ecosystem parameters have been affected by these changes in nutrient balance (Figure 12.2): copepod abundance changed from more than 75 percent to less than 30 percent of total mesozooplankton, zooplankton fecal pellets became a minor component of the in situ primary production consumed, and bottom-water oxygen consumption rates become less dependent on fast-sinking (diatom-rich) organic matter packaged mostly as zooplankton fecal pellets (Turner et al. 1998).

This coastal ecosystem can now shift from a food web composed of diatoms and copepods to one with potentially disruptive harmful algal blooms; the shift is controlled by Mississippi River water quality, which is in turn determined by land use practices far inland (Turner et al. 1998).

The second excellent illustration is the northwestern shelf of the Black Sea, which is under the direct influence of the Danube River, which discharges some 70 percent of the total freshwater to the Black Sea (Tolmazin 1985). From the 1960s to the late 1980s, DIN and DIP inputs increased by a factor of five and three, respectively, as a result of



**Figure 12.2.** Effects of fluctuating DSi:dissolved inorganic nitrogen (DIN) ratios in the Mississippi River on Louisiana shelf plankton food webs (from Turner et al. 1998). (a) Effects on copepod abundance, (b) effects on the contribution of fecal pellets to the total carbon in a surface sediment trap (5 m), (c) effects on the percentage of phytoplankton primary production captured as fecal pellets in a bottom sediment trap (15 m), and (d) effects on benthic respiration. LOOP and C6B denote stations from Turner et al. (1998).

human activities in the watersheds of main tributaries and along the shoreline (Cociasu et al. 1996). The consequent changes in DSi:DIN ratios of the Black Sea nutrient load appear to be larger than those caused by eutrophication alone; Humborg et al. (1997) suggested that the damming of the Danube, and in particular the construction of the Iron Gates Dam in the early 1970s, induced a decline in DSi concentrations (Figure 12.1) that could to explain in part the observed changes in nutrient balance. These changes are accompanied by a qualitative shift in the oxidation state of nitrogen compounds being delivered to the coastal areas caused by eutrophication in the freshwater reservoirs (Sapozhnikov 1992). Taken together, these changes have stimulated phytoplankton blooms of altered composition (Bodeanu 1992), especially toward non-siliceous mixotrophic species (Bologa et al. 1995; Bouvier et al. 1998). Cascading effects on pelagic (Bodeanu 1992) and benthic (Gomoiu 1992) food chains have been

observed, thought to be at the root of Black Sea ecosystem destabilization (Mee 1992; van Eeckhout and Lancelot 1997).

### Mesocosm Evidence Supporting the Paradigm

Mesocosms provide a means to manipulate nutrient concentrations and to study large volumes (several cubic meters) of water containing natural plankton communities. Since the late 1980s and early 1990s, mesocosm experiments have been designed to study the response of phytoplankton populations to varying nutrient concentrations and nutrient balance under different turbulence conditions (Estrada et al. 1988; Svensen et al. 2001), grazing pressure, or both (Alcaraz et al. 1988; Escavara and Prins 2002). With the increasing evidence linking changes in coastal water phytoplankton composition to changes in river Si:N ratios, mesocosm experiments specifically designed to study the influence of DSi on phytoplankton composition have flourished (Egge and Aksnes 1992; Wassman et al. 1996; Egge and Jacobsen 1997; Svensen et al. 2001; Svensen 2002; Roberts et al. 2003).

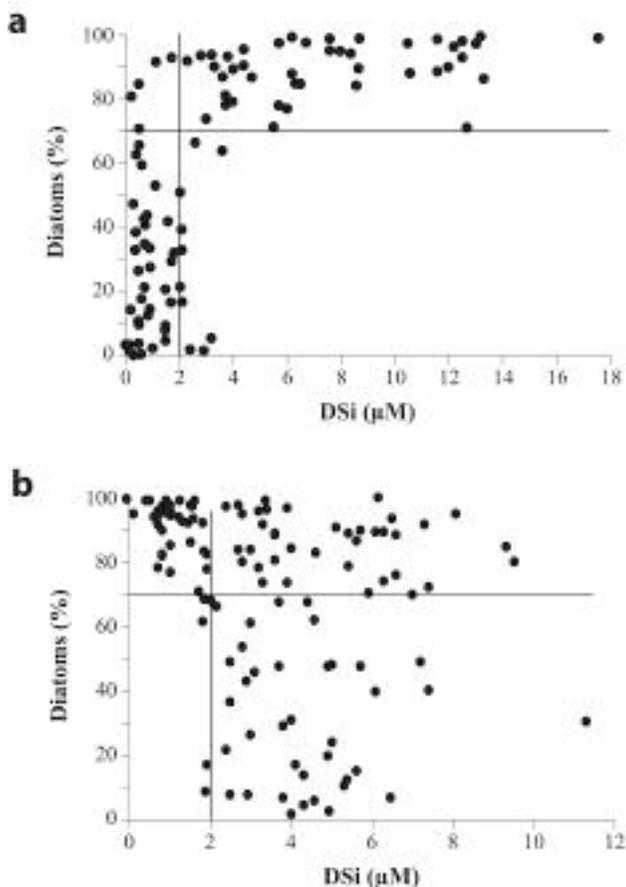
However, results from these experiments are somewhat contradictory. But the most cited study sustaining the paradigm we are interested in probably is the one by Egge and Aksnes (1992; Figure 12.3).

Using fourteen enclosures, these authors showed that diatom dominance (more than 80 percent of total cell counts) occurred irrespective of season if DSi concentration exceeded a threshold of approximately  $2 \mu\text{M}$ . They suggested that this could result from a higher maximum growth rate in diatoms at nonlimiting DSi concentrations (see also Martin-Jézéquel et al. 2000). Interestingly, this threshold is close to many  $K_s$  values measured in the field (see Chapter 9, this volume). It also corresponds to a threshold above which the BSi:CaCO<sub>3</sub> rain ratio increases sharply in the open ocean (Ragueneau et al. 2000). For all these reasons, this value of  $2 \mu\text{M}$  has become the standard value for DSi limitation. But the reality appears to be more complex, as seen from both mesocosm and field studies.

### Field and Mesocosm Evidence Against the Paradigm

The paradigm stipulates that DSi availability controls the shift from diatoms to non-diatom species, potentially harmful, with important implications in terms of carbon export toward both deeper waters and higher trophic levels.

The influence of DSi on the export toward higher trophic levels has been discussed indirectly in connection with the importance of diatoms in the food chain (Chapter 11, this volume). In a recent mesocosm study, Roberts et al. (2003) started their experiments with DSi concentrations higher than  $2 \mu\text{M}$ , and initially diatoms dominated, as found by Egge and Aksnes (1992). After Day 8 however, when DSi fell below  $2 \mu\text{M}$ , the relative contribution of diatoms to total autotrophic plankton biomass increased and continued to do so for 5 days. Similarly, in the field (Bay of Brest), Ragueneau et al. (1994) observed several diatom blooms in May and June 1992, while DSi concentra-



**Figure 12.3.** Contribution of diatoms to total phytoplankton as a function of DSi concentration. (a) Results from mesocosm experiments (Egge and Aksnes 1992). (b) Results from the Bay of Brest (France) (Fouillaron et al. submitted).

tions were far below  $K_s$  values and even close to zero. Two major reasons can be suggested to account for such observations.

First, the shift from diatoms to nondiatom species can be controlled by silicon regeneration, as suggested by Officer and Ryther (1980). Diatoms may be able to use immediately the DSi that is released from the dissolution of biogenic silica, so that DSi concentrations have no time to build up in the water column. Clearly, as discussed in Chapter 11, BSi production and dissolution fluxes should be measured in addition to DSi concentrations.

Second, the shift in phytoplankton composition may not be immediate because diatoms are known to exhibit some degree of flexibility when they become DSi stressed. Before the shift occurs, Roberts et al. (2003) observed physiological and biochemical changes of the dominant diatom species, such as differences in mean cell volume (MCV), C:MCV ratio, C:N ratio, and glucan concentrations. Laboratory studies have demonstrated that diatoms can sustain high growth rates despite low external DSi concentrations (Olsen and Paasche 1986; Brzezinski et al. 1990). In coastal waters, it has been observed that diatoms adjust to low DSi concentrations by thinning their frustules or decreasing the number and length of spines (Chapter 9, this volume). In the North Sea, Rousseau et al. (2002) observed that the Si:C ratio of the diatoms decreased with declining DSi concentrations during the productive season. This decrease was accompanied by shifts between diatom species. Thus, under increasing DSi stress, if the recycling flux becomes insufficient, diatoms exhibit a gradual response before a complete shift toward nonsiliceous species may occur.

In the summer of 1995, off the Danube River on the northwestern shelf of the Black Sea, the contribution of diatoms to total primary production was negligible, despite the fact that DSi concentrations were greater than 2  $\mu\text{M}$  (Ragueneau et al. 2002b). During that period, N and P limitations were preventing diatoms from blooming. A similar observation has been made by Lancelot et al. (2004) in the North Sea, with DIP again playing a major role in controlling the growth of summer diatoms. In the Bay of Brest and Chesapeake Bay, DSi clearly plays a critical role in spring (Ragueneau et al. 2002a, Conley and Malone 1992). But in summer, DSi builds up again in the water column because it is not being used up by diatoms. In the Bay of Brest in August and September, flagellates dominate while DSi concentrations increase steadily from near zero to more than 4  $\mu\text{M}$ . In this ecosystem, there are many diatoms in spring, when ambient DSi concentrations remain low, and there are no diatoms in late summer, when DSi concentrations build up again in the water column. This is illustrated in Figure 12.3, for direct comparison with the Egge and Aksnes (1992) mesocosm experiments.

Obviously, part of this discrepancy can be resolved by reasoning in terms of fluxes and not concentrations (Foullaron et al. submitted): DSi concentrations are low in spring because they are being used continuously by diatoms, whose growth rate must be controlled by the efficiency of DSi regeneration, which can be rapid if stimulated by bacterial activity (Bidle and Azam 1999). Diatoms can also acclimate to these low DSi fluxes by modifying their shape or silicification degree or by switching from one diatom species to another. DSi concentrations increase in summer because another factor prevents diatoms from using up the DSi stock. But the discrepancy is only partially relieved: These field observations clearly challenge the concept that diatoms would be better competitors for N and P when DSi concentrations are replete. In the North Sea or off the Danube River, low  $\text{PO}_4$  concentrations may explain the observations, because it has been shown that diatoms are poor competitors at low DIP concentra-

tions (Egge 1997), and flagellates can use P from organic sources. But why do diatoms dominate in the Bay of Brest in spring, when both DSi and DIP limit their growth (Del Amo et al. 1997)?

### *Nutrient Balance and the Development of HABs*

In a recent review of harmful algal blooms and eutrophication, Anderson et al. (2002) demonstrated the complexity of the response of coastal waters to nutrient enrichment. DSi is clearly playing a critical role, but it has to be seen as one controlling factor among others. To serve our purposes, a few examples of nutrient effects will be shown here.

Independently of DSi, the balance between N and P also plays an important role. In Tolo Harbor, Hodgkiss and Ho (1997) related the increasing amount of red tides between 1982 and 1989 to declining N:P ratios, from above Redfield to around 10:1. Similar observations were made by Romdhane et al. (1998) in Tunisian lagoons, with blooms of *Gymnodinium aureolumi*, and by Riegman (1995) in Dutch coastal waters, with blooms of *P. pouchetii*. As noted by Anderson et al. (2002), "The nutrient ratio concept has recently been expanded to include the relative abundance of different chemical forms of nutrients, such as organic versus inorganic N and C." The development of HABs has been related to the dissolved organic nitrogen components, particularly urea, as in Chesapeake Bay (Glibert et al. 2001). Several HABs have also been related to elevated ratios of dissolved organic carbon to dissolved organic nitrogen, such as the brown tides in Long Island (Lomas et al. 2001). In fact, it becomes clear that if diatoms are able to exploit nitrate-rich conditions (Goldman 1993; Chapter 11, this volume), microflagellates, including harmful dinoflagellates, are most often associated with low nitrate concentrations, higher ammonium, urea, or dissolved organic nitrogen supply, and consistent physiological preference for reduced N forms (Anderson et al. 2002 and references therein).

Just as some zooplankton species are able to switch from ambush to suspension feeding (Chapter 11, this volume), the ability of many flagellate species, including those forming HABs, to acquire their essential elements from both inorganic and organic (dissolved and particulate) sources provides them with an efficient survival mechanism. Although such mixotrophy has an energetic cost (need for both a photosynthesis apparatus and mechanisms for prey uptake and subsequent digestion; Rothhaupt 1996a, 1996b), it provides them with an enormous advantage when inorganic nutrients limit phototrophic growth (Tittel et al. 2003). With the improvement of methods to measure ingestion and C uptake, the importance of mixotrophy in the development of HABs becomes increasingly recognized (Anderson et al. 2002 and references therein). Note that another important capability of certain HAB species is to acquire some of their nutrients via extracellular oxidation or hydrolysis (Mulholland et al. 1998; Anderson et al. 2002 and references therein).

## Conclusion

Among the mechanisms proposed to explain silica depletion, some (e.g., increased diatom production through eutrophication and the artificial lake effect) are well established, whereas others (e.g., trapping of phytoliths behind dams, loss of vegetated soils with damming, and increased BSi retention with increasing biodeposition) clearly deserve more research.

Numerous field and experimental studies (mesocosms) have related the shift from diatoms to nondiatom species, potentially harmful, to declining DSi:DIN and DSi:DIP ratios. But the relationship between DSi availability and diatom importance is not straightforward. A good illustration of this is the response of the Bay of Brest ecosystem to nutrient enrichment and declining DSi:DIN nutrient ratios, without any systematic shift from siliceous to nonsiliceous species. Whether this can be attributed to physical (Le Pape et al. 1996; Le Pape and Menesguen 1997) or biological (Chauvaud et al. 2000; Ragueneau et al. 2002a) factors is still under debate. Specifically related to Si cycling (e.g., in the Bay of Brest ecosystem), the interactions between nutrient enrichment and damming, for example, or between nutrient enrichment and the proliferation of an exotic species (*C. fornicata*) that acts as the biological component of the filter were found to modulate the effect of nutrient enrichment.

Whereas eutrophication is being reduced in Europe and the United States, it is increasing in Southeast Asia with growing population demand. There, major rivers are being dammed at accelerating rates (Milliman 1997), and aquaculture is flourishing to satisfy food demand (Ruiz et al. 2000). Thus, drastic reductions in DSi fluxes to the ocean might occur in this region, which plays a critical role in land–ocean fluxes of dissolved and particulate matter in general (Milliman and Maede 1983) and for DSi in particular (Ittekkot et al. 2000).

It is difficult to determine the extent to which anthropogenic inputs of DSi may compensate for the observed reductions in DSi fluxes. In addition, little is known about changes in the production and weathering of Si with changes in land use (Likens et al. 1970). The long-term effects of disturbance with agriculture and the more recent effects of acid rain on weathering, and thus the production of DSi, also are unknown.

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