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Coastal eutrophication near the Mississippi river delta

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CHANGES in delivery of river-borne nutrients such as dissolved phosphate, nitrate and silicate, owing to land-use changes and anthropogenic emissions, are known to result in eutrophication¹—enhanced phytoplankton blooms—and more severe hypoxic events^{2–4} in many enclosed bays and seas. Although similar ecological effects might be expected on continental shelves, the occurrence of such eutrophication has remained unresolved⁵. Here we present evidence of eutrophication of the continental shelf near the outflow of the Mississippi river, obtained by quantifying biologically bound silica (BSi) in diatom remnants within dated sediment cores. BSi accumulation rates are greatest in water depths of 20 to 50 m within 100 km of the river mouth, and have increased by as much as 100% this century. The increases were substantial by 1980, by which time riverine nitrogen loading had doubled relative to the beginning of the century, even though the silica loading had declined by 50% over the same period. Thus changes in river-borne nutrient loadings can modify coastal food webs and affect the amount and distribution of oxygen in bottom waters on the scale of continental shelves.

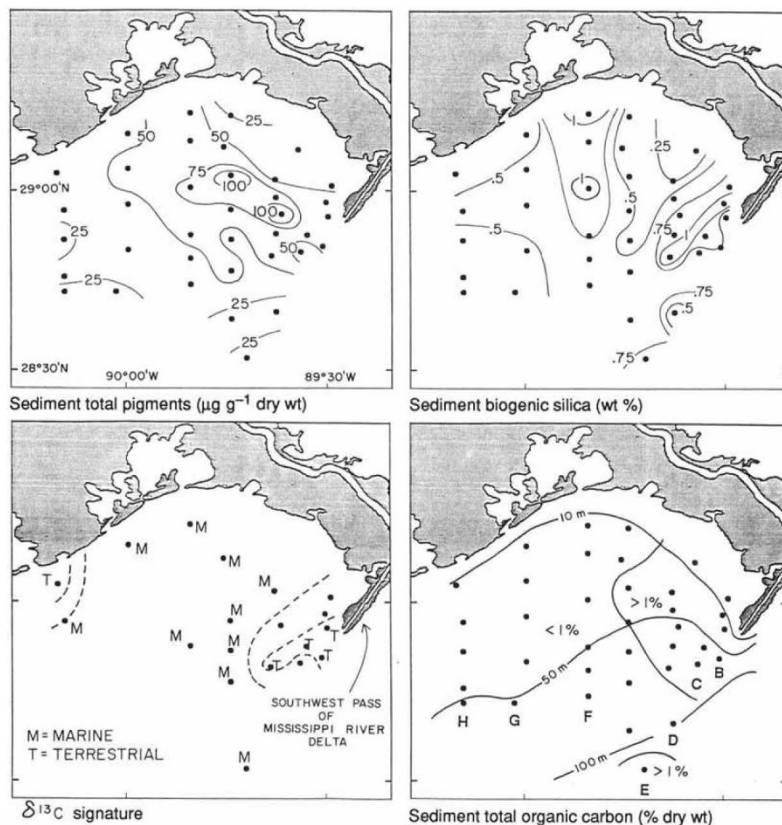
The Mississippi river, the largest river of the North American continent, drains 40% of the conterminous United States, and is third, sixth and eighth largest in the world in terms of length, sediment yield and discharge, respectively⁶. Land-use changes this century have resulted in a doubling of dissolved nitrate concentration and a halving of dissolved silicate concentration⁵.

These changes and the resulting decline in the annual average dissolved Si:N (as silicate and nitrate) atomic ratio (from 4:1 to 1:1) could have significantly affected diatom growth, intra-specific competition and production^{1,2,7}, but interpreting these results yields ambiguous answers. For example, silicate concentrations along the river-to-sea-water gradient of the Mississippi river mixing plume were analysed for samples collected after 1950. The net uptake of silicate at 30‰, towards the end of the mixing plume on the continental shelf, has remained at a similar, or perhaps at a higher level after 1979, than before 1979 (ref. 8). This result suggests that the net silicate uptake at the seawater end of the mixing plume did not decline after the 1960s when the dissolved silicate concentration fell and the dissolved nitrate concentration began to rise. In contrast, Schelske *et al.*⁹ described a relevant sequence of events in the Great Lakes, wherein increased nutrient loading (primarily phosphorus) initially stimulated diatom production rates. Diatom production subsequently declined as the silica necessary for diatom growth became limiting when the BSi was buried, rather than recycled into the water column. The new steady-state conditions resulted in lower diatom production than before eutrophication.

Many estuaries and several enclosed bays and seas (the Adriatic, the Baltic, the Black Sea and Chesapeake Bay) are known to be undergoing nutrient enrichment owing to anthropogenic influences within the watershed^{1,3,4}. But because of the substantial differences in physical characteristics and processes (such as shoreline length, flushing and wave energy) between open and enclosed coasts, it is by no means obvious that the biological effects of increased riverine nutrient loadings to open coastal waters—the case considered here—will be comparable to those seen off enclosed coasts. Two different hypotheses have been advanced⁵ to predict the possible changes in the phytoplankton community around the Mississippi outflow since the 1950s: that the productivity of coastal phytoplankton is limited by nitrogen, not silica, so that higher nitrogen loading will result in proportionally higher phytoplankton production rates; and, that the combination of lower riverine silica fluxes and a Si:N

FIG. 1 The spatial distribution in April 1989 of total phytoplankton pigments, biologically bound silica (BSi), $\delta^{13}\text{C}$ signature and total organic carbon in sediments beneath the Mississippi river delta plume.

METHODS. Surface sediments were collected by a 0.25-m² spade corer (General Oceanics). Chlorophyll *a* and phaeopigments were determined fluorometrically, before and after acidification, on the upper 5 mm of sediments after 24-h extraction in 90% acetone and combined for total¹⁹. The upper 5 cm was used for total organic carbon (Control Equipment Elemental Analyzer), BSi (ref. 20) and $\delta^{13}\text{C}$ signature (automated Deltas mass spectrometer; the Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts). $\delta^{13}\text{C}$ values < -22.2‰ indicate terrestrial (T) inputs to sediments, values of -20.4 to -21.44‰ indicate marine (M) inputs, and intermediate values indicate no clear signal (unlettered) (ref. 21; B. Fry, personal communication). Letters B to H on sediment TOC diagram indicate transects.



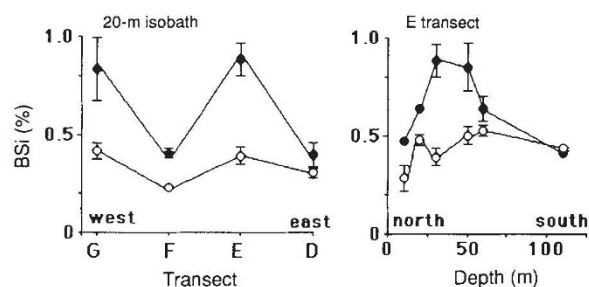


FIG. 2 The concentration of BSi in sediments along a 20-m isobath transect west of the Mississippi river delta (transects D to G) (left) and perpendicular to shore along the E transect (right). The average concentration of BSi in sediments for two different time periods is shown: between 1900 to 1960 (hollow circles), and after 1980 (solid circles). The error bar is ± 1 standard error. Values for the transition period of 1960 to 1980 are excluded. Sediments collected from 20 m water depth and ~ 20 km westward of transect H were exposed former deltaic deposits that are not presently accumulating sediments. Transect letters are the same as in Fig. 1, sediment TOC diagram.

ratio near 1:1 will result in lower phytoplankton production rates through limits on diatom production.

We investigated whether a pattern of historical eutrophication was identifiable in the continental shelf sediments influenced by the Mississippi river. We collected sediment cores from the Mississippi river delta bight (Fig. 1) during April 1989. Sample locations are from the region of locally high sedimentary carbon, sediment phytoplankton pigments from *in situ* phytoplankton production (marine origin), and BSi (1% total organic carbon (TOC), $28.1 \mu\text{g g}^{-1}$ dry weight and 0.6% BSi, respectively). This

sediment signature, directly downstream and beneath the surface riverine/estuarine dilution plume, reflects the *in situ* primary production and subsequent transport of organics from surface to bottom waters very near the river delta. Where a terrestrial signal of sediment carbon is indicated (Fig. 1), the higher concentration of BSi in surface sediments may be related to the presence of freshwater diatoms that contain ten times more silica per cell volume than marine diatoms¹⁰.

The concentration of BSi in these sediments ranged from 0.15% to 1.3%, and was highest in 25–50 m water depth (Fig. 2) in the middle of the sampling area. Sedimentation rates within 50 km of the river delta are $0.5\text{--}2 \text{ cm yr}^{-1}$ and generally $<0.3 \text{ cm yr}^{-1}$ further away from these sampling stations. Thus, the total annual deposition rates of BSi on this shelf are highest in the middle of study area. The best detail was gained using data from cores collected at intermediate depths (27–50 m), where both the BSi concentration and accumulation rates are highest (Fig. 3). Coincidental changes in the BSi concentration with time are evident, especially in the 1955 to 1965 period (a rise and fall) and a post-1975 (1980?) rise. The BSi concentration in sediments from deeper waters were generally stable through time.

The average concentration of BSi in sediments dated after 1980 is higher than for those dated between 1900 and 1960 (Figs 2–4). Sediments dated before 1900 have, on average, the same concentration of BSi as those dated between 1900 and 1960 (Fig. 4). The enhancement of BSi concentration in 15 sediment cores dated after 1980 is up to 43% higher than in sediments dated between 1900 and 1960.

The general pattern that emerges is an equilibrium accumulation of BSi from 1800 to 1900, then a slow rise, followed by a more dramatic rise in the past two decades. Coincidental variability about decadal averages exists among the sampled environments, implying shelf-wide water mass mixing and conservative accumulation of buried diatom frustules. The pattern in changes of BSi concentration parallels the documented increases in nitrogen loading in the lower Mississippi river (Fig. 3c). But nutrient data are sparse before the 1950s, and exist for only four other years (1905–06 and 1933–34) this century.

The organic carbon accumulation rate in the middle of these sample sites during the 1980s is $90 \text{ g-C m}^{-2} \text{ yr}^{-1}$ (the estimate is based on sedimentation rates and % carbon of the sediment cores), or $\sim 31\%$ of the estimated annual phytoplankton production rate of $290 \text{ g-C m}^{-2} \text{ yr}^{-1}$ (ref. 11). If the assumption is made that the BSi:C ratio at the time of deposition remained constant this century, then the increased BSi deposition after 1980 represents $\sim 40 \text{ g-C m}^{-2} \text{ yr}^{-1}$, and is thus a significant change in carbon deposition rates.

The ecological implications of the increased BSi deposition rates since 1980 include effects on continental shelf food webs and on bottom waters with severe oxygen deficiency. The effects on the diatom community of increased riverine loading of nitrogen probably compensated for the decreased loading of silica. Because the altered N:P:Si atomic ratios and loadings are known to differentially confer competitive advantages among

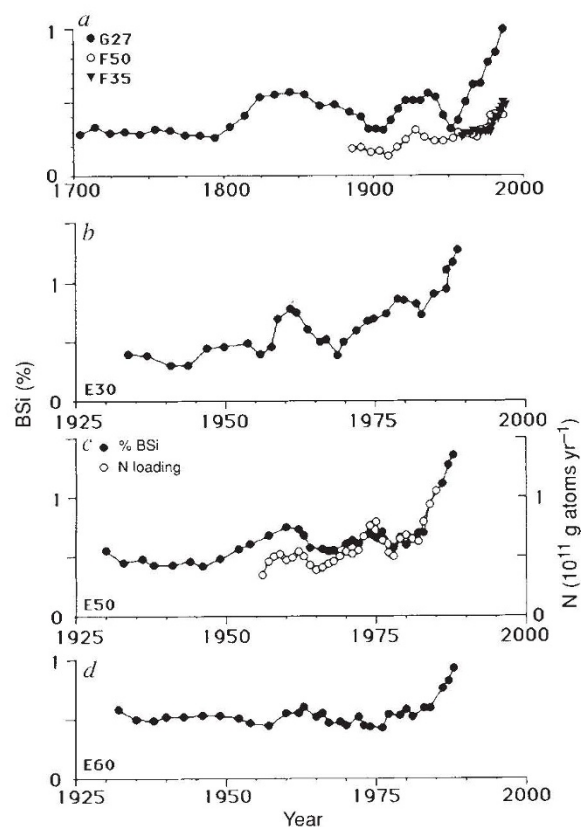


FIG. 3 The average concentration of BSi in sediments in each section of six dated sediment cores from stations at intermediate station depths (between 27 and 50 m). The letter and number code for each station are the transect and station depth, respectively. a, Data for three cores from transect F and G for the periods shown. b, c, d, Data for cores from transect E for 1925 to present, at depths of 30, 50 and 60 m, respectively. A 3-yr running average for each sampling data is shown. The data for station E50 (c) are plotted with the 3-yr running average of the nitrogen loading from the Mississippi river through the delta passes⁶. Transect letters are the same as in Fig. 1, sediment TOC diagram.

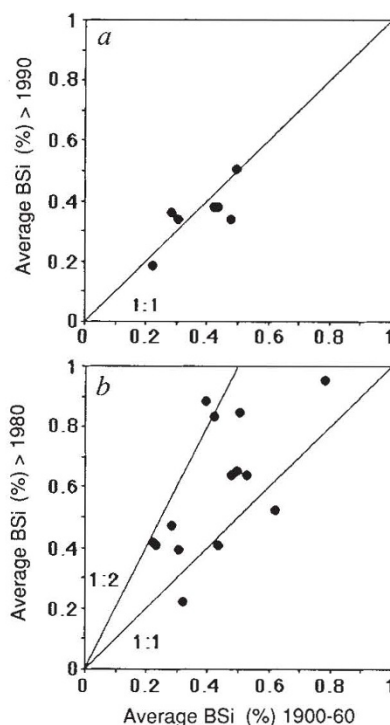


FIG. 4 The concentration of BSi in sediments dated in one interval compared to that in other intervals. *a*, Plot of the average BSi concentration of sediments dated before 1900 against that of sediments dated between 1900 and 1960 (8 stations). *b*, Plot of the average BSi concentration of sediments dated after 1980 against that of sediments dated between 1900 and 1960 (15 stations).

various diatoms and non-diatoms^{1,2,12}, these changes should affect both phytoplankton consumers and the rest of the continental-shelf food web. The implication of these results for interpreting the probability of increased severity of hypoxic (dissolved oxygen $<2 \text{ mg l}^{-1}$) events and/or duration is particularly significant. Hypoxic water masses during the summer extend over an area of up to 9,000 km² on the inner continental shelf, and represent the largest hypoxic zone in the Western Atlantic^{13,14}. This oxygen deficiency is due both to the effects of water column stratification that restricts vertical reaeration and to the respiration of organic material derived mostly from *in situ* sources (for example, phytoplankton). These hypoxic areas have low densities of fish and invertebrate fauna¹⁴⁻¹⁸. Diatom remains are extensive in surface sediments and in bottom layer sediment traps located 30 km west of the study area (N. Qureshi and Q. Dortch, personal communication; N.N.R., unpublished data). These remains are derived directly or indirectly from *in situ* phytoplankton production. We conclude from these analyses that the organic flux of diatoms from surface to bottom waters beneath the Mississippi river plume increased this century. These changes coincided with changes in riverine nitrogen loadings and resulted in higher organic sedimentation in bottom-water layers. The depletion of bottom-water oxygen and its persistence and areal coverage on this shelf is thus indicated to have been altered this century. Because of the close coupling between riverine loading and phytoplankton production, reversal of these effects is possible to the degree that water quality changes are altered. However, the management of one nutrient (Si or N) may not be sufficient to reduce eutrophication to an acceptable amount if the compensatory qualitative adaptations of species lead to new phytoplankton communities, including those with noxious or toxic species. □

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Worldwide occurrence of silica-rich melts in sub-continental and sub-oceanic mantle minerals

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Rock samples derived from the Earth's upper mantle commonly show indirect evidence for chemical modification. Such modification, or 'metasomatism', can be recognized by the precipitation of exotic minerals such as phlogopite, amphibole or apatite¹, and by the overprinting of the bulk compositions of the mantle rocks by a chemical signature involving the enrichment of potassium and other 'incompatible' elements². Here we study the composition of the metasomatic agents more directly by examining melt and fluid inclusions trapped in mantle minerals. These inclusions are secondary, forming trails along healed fracture planes. A systematic study of the chemical compositions and entrapment temperatures and pressures of inclusions from 14 ultramafic peridotites from both continental and oceanic intraplate regions shows that volatile- and silica-rich metasomatic melts are present throughout the lithosphere. Their compositions, which differ dramatically from those of erupted, mantle-derived magmas, are more akin to continental than to oceanic crust.

The xenolith samples come from the Society Islands (Tahaa, Tahiti), Canary Islands (Lanzarote, Hierro), Kerguelen Island (Jeanne d'Arc Peninsula), Comores Island (La Grille), New Mexico (Kilbourne Hole), Arizona (San Carlos), Germany (Dreiser Eifel), Italy (Mt Iblei), France (Massif Central), Mon-