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Fixation of dissolved silicate and sedimentation of biogenic silicate in the lower river Rhine during diatom blooms

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Abstract. Concentrations of dissolved silicate and particulate biogenic silicate were measured in three branches of the lower river Rhine in The Netherlands in order to analyse the role of this element in the eutrophication of the river basin. Particulate silicate followed the seasonal development of the phytoplankton, which was dominated by diatoms. The concentration of dissolved silicate fell during blooms ($< 0.1\,mg.l^{-1}$), but the amounts of biogenic silicate measured ($\sim 1\,mg.l^{-1}$) were insufficient to explain the seasonal decrease in the dissolved fraction; this indicates retention of silicate upstream. Some particulate biogenic silicate in river water settled in man-made sedimentation areas in the Rhine delta. The observations suggest that changes in silicate fixation in the Rhine may have contributed to the incidence of non-diatom phytoplankton blooms in receiving waters.

Introduction

The fluxes of phosphorus, nitrogen, sulphur and silicon are closely linked, both in sea water (Wollast 1981) and in fresh water (Schindler 1981). As rivers form an essential link between the cycles of elements in catchment areas and coastal waters, the increased riverine loads of nitrogen and phosphorus have also affected other elemental cycles (such as that of silicon) in receiving waters (Officer & Ryther 1980).

Van Bennekom et al. (1975) suggested that eutrophication of Dutch coastal waters, brought about by high loads of nitrogen and phosphorus in the river Rhine caused silicate to become limiting for diatoms. Depletion of silicate in these coastal waters may favour the formation of blooms of algae that do not require silicate, such as the flagellate *Phaeocystis* sp. (cf. Veldhuis et al. 1986). Analogously, for more than a decade Dutch inland waters exposed to Rhine water have frequently experienced blooms of cyanophytes (cf. Berger & Sweers 1988). In view of the adverse biological conditions that generally accompany these algal blooms it seems necessary to explore the fate of riverine silicate and to investigate its role in the natural silicate cycle of receiving waters.

Silicate concentrations have been measured in many rivers and decreases in the concentrations of dissolved silicate have often been associated with diatom growth (Müller-Haeckel 1965; Swale 1969; Lack 1971; Wollast & De Broeu 1971; Edwards 1974; Wollast 1978; Admiraal et al. 1989). However, the concentrations of biogenic silicate immobilized by river diatoms have been measured only indirectly (Wang & Evans 1967) and therefore the riverine discharges of particulate biogenic silicate are largely unknown. In the research reported in this paper we attempted to establish the importance of particulate biogenic silicate in the river Rhine as compared with dissolved silicate. Furthermore, we analysed the relation of particulate silicate to plankton growth and to sedimentation in the delta of the river Rhine in order to evaluate the role of silicate in receiving waters.

Materials and methods

Figure 1 shows the location of the sampling stations in the Dutch section of the lower river Rhine. In 1987 the Maassluis station (Rhine km 1019), on the main branch of the river (the Rotterdam Waterway), was sampled fortnightly at outgoing tide. Surface waters were collected with a bucket either in the middle of the stream (Jan.–Aug. 1987) or by pooling samples taken across a cross-section of the river (Sept.–Dec. 1987). Salinity measurements showed that admixture of seawater was less than 5%. A more detailed account of the observations on Rhine plankton in 1987 is given by de Ruyter van Steveninck et al. (1989).

In 1988 three branches of the Rhine were sampled five times, while "following" a body of water during its transport from the Lobith station through The Netherlands (Fig. 1). Observations were started on April 17 (week 16), May 15 (week 20), June 12 (week 28), July 10 (week 28) and August 7 (week 32). The assumed residence time of water in the truly riverine sections (e.g. 41 h down to station km 995, 45 h down to station km 989 and 24 h down to station km 961) was based on mean discharge data provided by the Department of Public Works. The downstream stations Ketelmeer (km 1005), Maassluis (km 1019) and km 1000 (Fig. 1) were sampled after respectively 96, ca. 58 (depending on tide), and 72 h. Sedimentation of suspended materials may be expected in the lowest reaches of all three branches. The lower station 1005 on the river IJssel is essentially part of the lake IJssel; the lower station 1019 in the Rotterdam Waterway is located at the deep tidal reach of the river, where the suspended matter concentrations

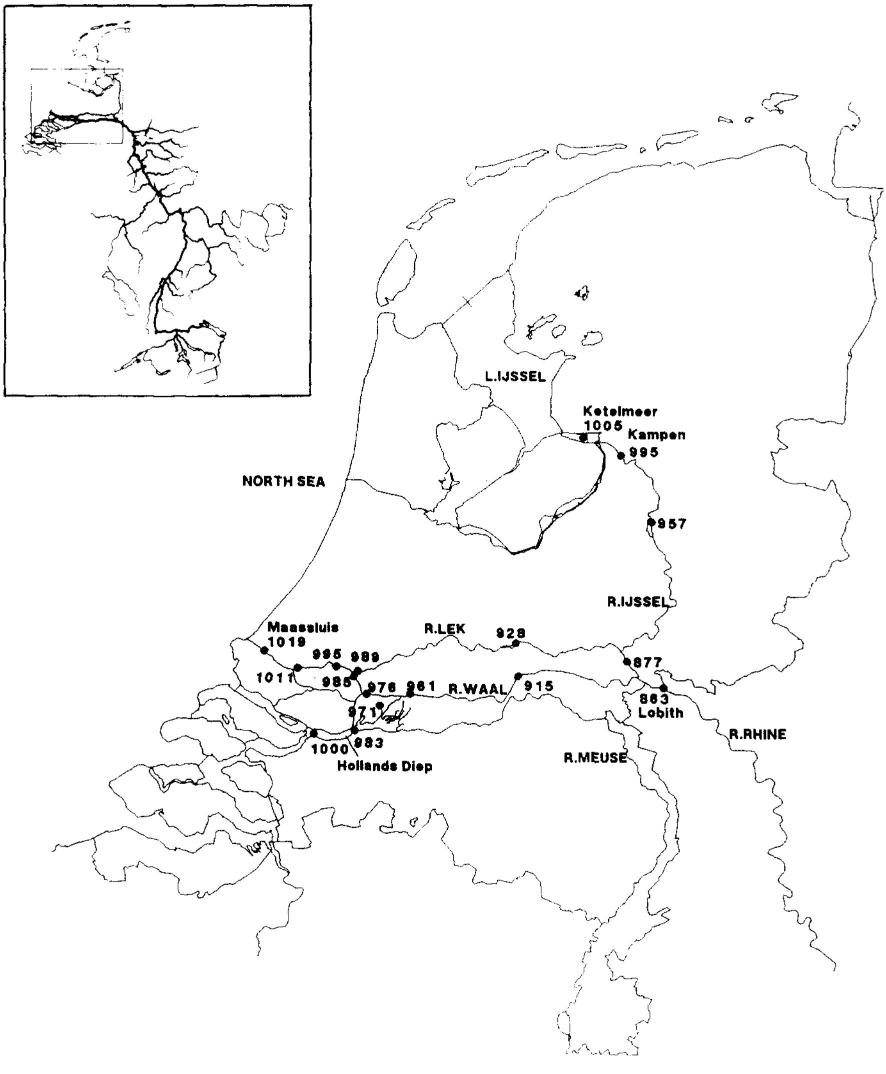

Fig. 1. Location of sampling stations in the three branches of the lower river Rhine in the Netherlands. River IJssel: Lobith-Ketelmeer; river Waal; Lobith-Hollands Diep; river Waal/Lek: Lobith-Maassluis.

are generally lower than further upstream. In the southern branch of the Rhine, the river water flows into the basin Hollands Diep; the now closed estuary of the Rhine. The cross section of the river or sedimentation area was sampled, mostly from a ferry, by pooling 6 buckets of water, two from near the left bank, two from near the right bank, and two in the middle of the river. Observations made in 1988 on plankton development and on several abiotic parameters will be published elsewhere.

Dissolved reactive silicate was measured by the molybdate-ascorbic acid method using an autoanalyser (Technicon Industrial Systems, Silicates in water and seawater, Industrial Method no. 186-72W, Terry Town, NY, 1973). To determine the silicate content of particulate material 0.3–0.7 l. was filtered on 0.45 μm cellulose acetate membrane filters (Sartorius) in 1987 or 0.45 μm polycarbonate filters (Nucleopore) in 1988. The filters were hydrolysed in 18 ml 0 5% solution of Na_2CO_3 at 85 °C for 2 h. When cool, the extract was neutralized with 0.5 N HCl and the silicate concentration was measured as described for dissolved silicates. Krausse et al. (1983) tested this procedure, taken from Paasche (1980), and compared it with other methods. They recommended wet-alkaline digestion methods for routine analysis of biogenic silicate in suspended matter in preference to infra-red analysis, alkaline fusion and hydrofluoric acid/nitric acid methods. The use of cellulose-acetate filters in the tentative series of observations in 1987, resulted in blank values that were higher than when polycarbonate filters were used. However, all measurements were corrected for background silicate. Chlorophyll *a* concentrations were determined in extracts (80% ethanol, 75 °C) of glassfibre-filtered material larger than 0.3 μm (Schleicher & Schuell, no. 6). Extinction was measured at 665 and 750 nm before and after addition of 4 mM HCl. The concentration of chlorophyll *a* was calculated following Nusch and Palme, 1975 (NEN, Netherlands Standards Method).

Dry weight and ash-free dry weight of suspended material were determined using pre-weighed (1.5 h, 75 °C), cellulose acetate filters (Sartorius SM 12303, pore size 1.2 μm). Dry weights were measured after 1 h drying at 75 °C; subsequently filters were combusted at 600 °C for 45 min, after which the ash was weighed.

Results

Figure 2 shows the seasonal variation for 1987 in dissolved and particulate biogenic silicate in the main branch of the Rhine at Maassluis just before the river debouches into the North Sea. Periods with low values of dissolved silicate were evident in the spring and the summer. The concentrations of particulate biogenic and dissolved silicate showed opposite trends. However, the maximum in the biogenic silicate (ca. 0.3 mg $Si.l^{-1}$) did not account for the decrease of dissolved silicate by ca. 3 $mg.l^{-1}$ below winter values. The concentrations of particulate biogenic silicate (y) correlated positively with chlorophyll *a* (x; $y = 0.0217\,x + 0.116$, $r = 0.79$ $n = 12$ $p < 0.01$). One extremely turbid sample with a dry weight of 90 $mg.l^{-1}$ produced a slightly

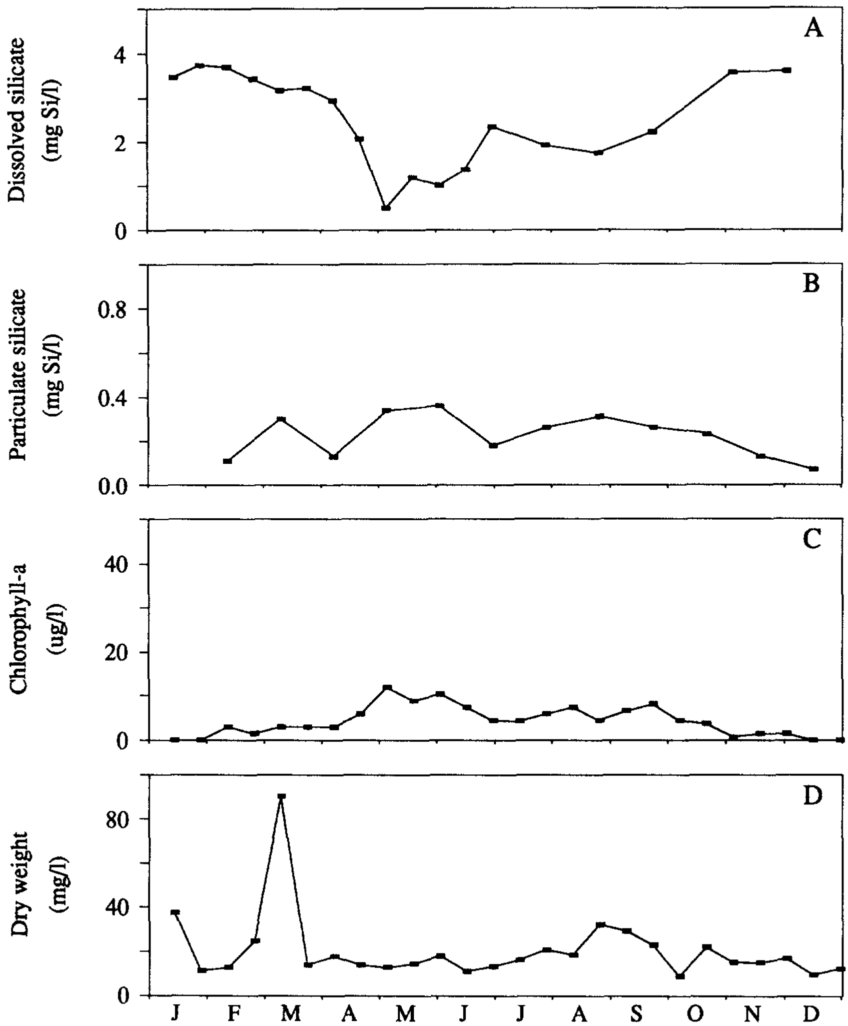

Fig. 2. Seasonal variation in: dissolved silicate (A); particulate, biogenic silicate (B); chlorophyll *a* (C); and suspended dry weight (D), at the Maassluis station in 1987.

elevated value of particulate silicate (Fig. 2). The Maassluis station is in the tidal reach of the Rhine and despite the sampling at outgoing tide some estuarine influence, such as resuspension of accumulated particles, may occur.

Since the observations in 1987 indicated a relationship between silicate fractions and phytoplankton development in the river, more detailed observations were carried out in 1988. Figure 3 shows the changes in silicate fraction in Rhine water observed during transport in three branches of the

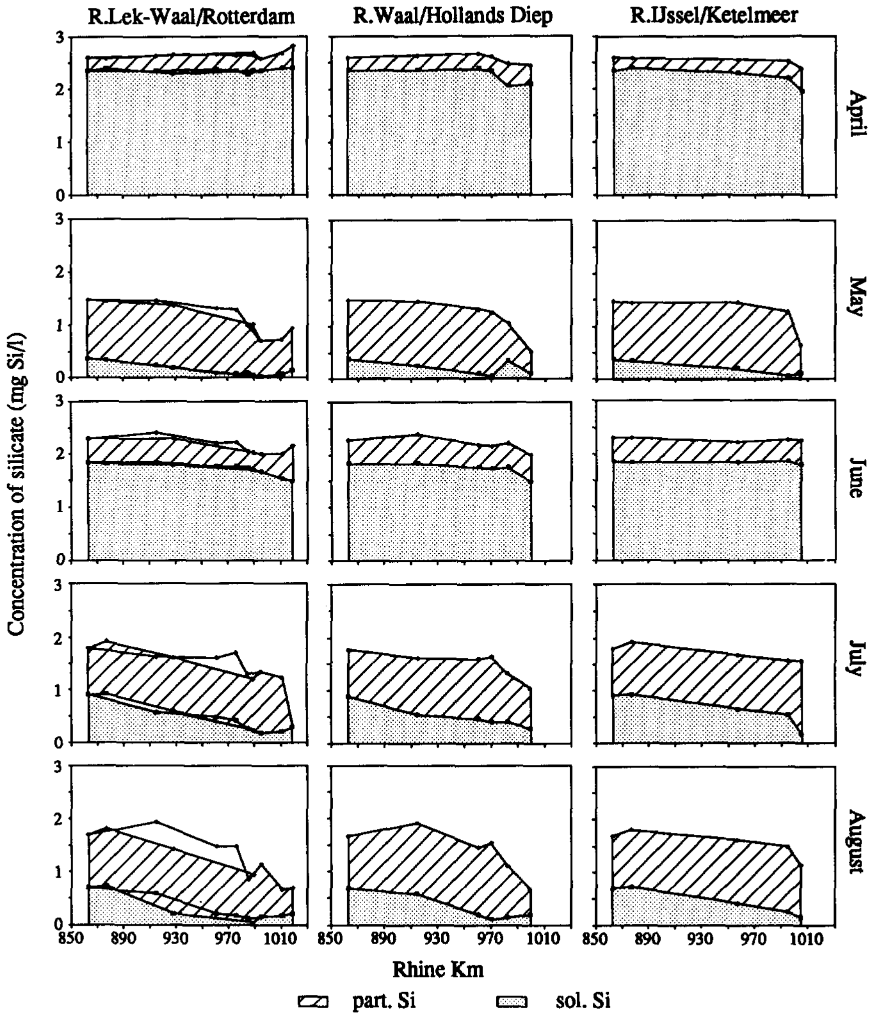

Fig. 3. Changes in the concentration of dissolved silicate and of particulate, biogenic silicate during transport of water through three branches of the river Rhine, observed on five occasions. Particulate silicate is plotted on top of dissolved silicate. Double lines for the Lek/Waal reach indicate the contribution of both rivers before confluence into the Rotterdam Waterway.

river. These observations were carried out during the 1988 growing season. On two occasions, in April and June, the initial chlorophyll *a* values of respectively 6 and 10 $\mu g.l^{-1}$ at Lobith station indicated a very sparse phytoplankton. On the other occasions a dense phytoplankton population, dominated by diatoms, were present and the chlorophyll *a* concentrations amounted to 52, 47 and 55 $\mu g.l^{-1}$ in May, July and August respectively.

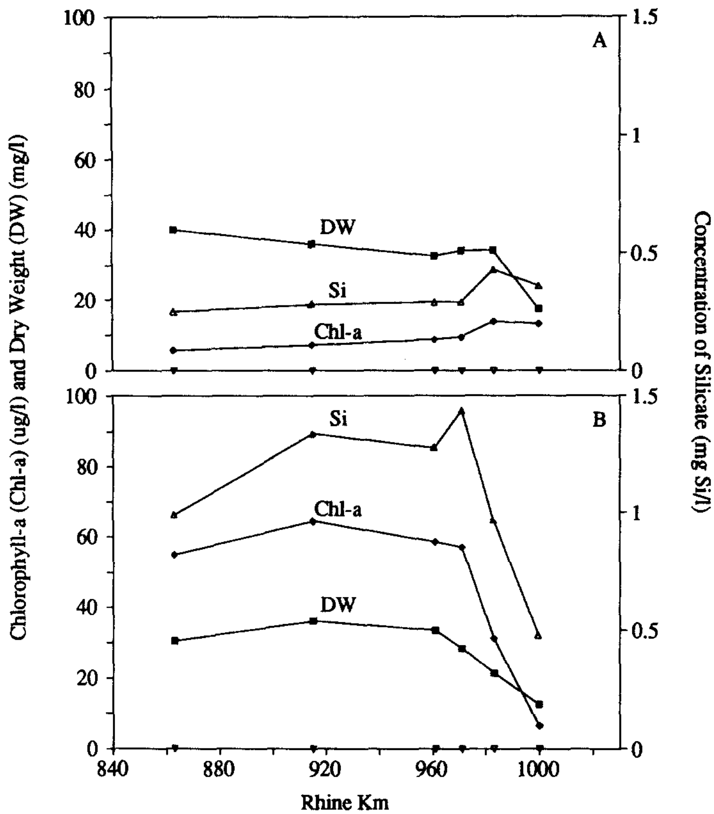

Fig. 4. Changes in the concentrations of suspended dry matter (DW), chlorophyll *a* (Chl-a) and particulate, biogenic silicate (Si) during transport of Rhine water in the R. Waal and Hollands Diep. A: April 1988, B: August 1988.

During the three bloom periods the concentration of particulate biogenic silicate exceeded that of dissolved silicate. The depletion of dissolved silicate continued during transport; ultimately values below $0.1\,mg.l^{-1}$ were reached. During the non-bloom conditions (April, June) dissolved Si was slightly reduced during transport of river water, consistent with the slight growth of the phytoplankton as indicated by increasing chlorophyll *a* values (Fig. 4a).

In nearly all cases the sum of dissolved and particulate biogenic silicate decreased during the course of transport in the river reaches. The exceptions are restricted to stations in the tidal range of the river. The particulate silicate fraction was particularly reduced in the downstream reaches of the river branches (the sedimentation areas) during blooms. The dry weight of suspended material also tends to decrease in these areas, but the particulate

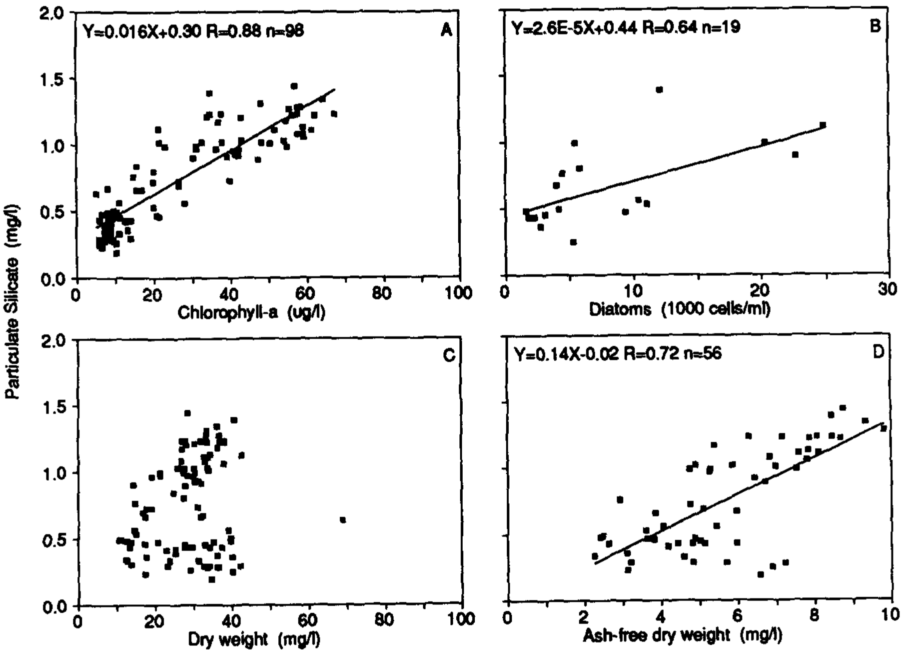

Fig. 5. Relations between particulate, biogenic silicate and chlorophyll *a* (A); number of diatom cells (B); dry-weight of suspended matter (C); and ash-free dry weight (D). All data from 1988.

silicate seems to follow the chlorophyll *a* concentrations rather than those of suspended matter (Fig. 4). Comparison of all the data from 1988 shows that particulate silicate correlates positively with chlorophyll *a* and with the less numerous diatom cell counts that were only available for the Lobith, Ketelmeer, Maassluis and km 1000 stations (Fig. 5). The dry weight of suspended matter did not correlate with particulate silicate, consistent with the assumption that our determination of particulate silicate was specific for biogenic silica. In contrast, the ash-free dry weight did correlate with plankton density in the river and hence correlated well with particulate silicate (Fig. 5).

Discussion and conclusions

These observations show that during the 1987 and 1988 growing seasons a high fraction of the silicate load of the river Rhine is contained in phytoplankton. Concentrations of biogenic silica of 2 $mg.l^{-1}$ were also found in the Illinois River (Wang & Evans 1967), although these were estimated indirectly via determinations on filtered and unfiltered samples.

The depletion of dissolved silicate in several English rivers, coinciding with diatom blooms, (Swale 1969; Lack 1971; Edwards 1974) also suggests that biogenic silicate conveys a significant part of the river's silicate load to the sea in spring and summer. For the river Rhine, Friedrich & Müller (1984) contend that there has probably been a strong increase in the diatom concentrations during the last 80 years and they suggest that the most likely cause is eutrophication. If this is correct and less silicate was incorporated by a smaller diatom population the concentration of dissolved silicate during the summer at the beginning of the century may have been even higher than van Bennekom et al. (1975) assumed in their study of the riverine nutrient input into the North Sea.

Diatom development in rivers is only one aspect of the rivers silicate budget. For example, eutrophication of the Swiss lakes that feed the river Rhine has caused an increased silicate fixation in the epilimnetic diatoms (Sommer 1986) leading to pronounced sedimentation of particulate silicate on these lake bottoms (Stabel 1985). Thus, silicate retention already occurs in upstream sections of the river Rhine: the pre-alpine lakes. This may also explain why in the present study the sum of dissolved and particulate silicate in the lower course did not reach the winter values of dissolved silicate.

In the river Rhine the concentration of dissolved and biogenic silicate diminished within observation periods of one week (this study). In lake IJssel, which receives ca. 15% of the Rhine water, much of the riverine dissolved silicate disappears in summer (van Bennekom et al. 1974) and estuaries are also known as sinks of riverine silicate (Peterson et al. 1985; Nixon 1987). Deposits of particulate silicate can be subject to intense remobilization (Bailey-Watts 1976; van Bennekom et al. 1974), but biogenic silicate is also known to be immobilized by high concentrations of metal ions, e.g., aluminium (Lewin 1961; van Bennekom 1981). As metal ions are discharged in large quantities by the river Rhine, the remobilization rate of biogenic silicate in this river is uncertain. Silicate is usually supplied in plentiful amounts to flood plains, estuaries and coastal seas through land weathering and river discharge. This is evidently no longer the case in the waters affected by the eutrophic Rhine. Both in the coastal North Sea water (van Bennekom et al. 1975; Veldhuis et al. 1986) and in Dutch inland waters, the spring bloom of diatoms is nowadays restricted by the concentration of silicate present after the winter. Indeed, silicate additions to late spring diatom blooms enhanced the development of these algae in incubated North sea water (van Bennekom et al. 1975) and in lake water (Moed et al. 1976). Exhaustion of silicate while nitrogen and phosphorus are still present is probably responsible for the extensive blooms of *Phaeocystis* in the coastal waters (Veldhuis et al. 1986) and may contribute to the widespread occurrence of cyanophyte blooms in inland waters (Berger & Sweers 1988). This, then, is in accordance with the viewpoints of Officer and Ryther (1980) who suggest that the change from diatom- to flagellate- (or non-diatom) dominated communities is governed by the relative magnitudes of silicon, phosphorous, and nitrogen fluxes to receiving waters. In the case of the river Rhine the greatly increased loads of nitrogen and phosphorus may have caused similar community changes in the delta region. On the other hand, the successive removal of silicate by diatoms in pre-alpine lakes, the development of a dense river plankton, and the creation of artificial sedimentation areas in The Netherlands may have accelerated the changes from diatom-based communities to flagellate or cyanophyte-based communities. Recent blooms of *Chrysochromulina polylepis*, causing fish-kills in Scandinavian waters, have also occurred in waters depleted of silicate (Workshop on eutrophication on algal blooms in North Sea coastal zones, the Baltic and adjacent areas, Oct. 26–28, 1988, Brussels; L. Edler). This phenomenon may also be caused by nitrogen and phosphate inputs that are high with respect to the available silicate. If the views on the role of the silicon cycle expressed here and in Officer and Ryther (1980) are correct, the carrying capacity of natural waters for phosphorus and nitrogen inputs should be re-examined.

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