RESEARCH PAPER

Increasing dissolved silica trends in the Rhine River: an effect of recovery from high P loads?

Jens Hartmann · Jason Levy · Stephan Kempe

Abstract The development of river dams and further human activities (causing increased nitrogen (N) and phosphorus (P) nutrient loads), are responsible for a decline in dissolved silica concentrations (DSi) in many river systems. Here, the impact of the reduction of N- and P-concentrations on DSi is examined for the Rhine River. During the last decade of the twentieth century, annual average DSi concentrations increased by $\sim 70\%$ in the Rhine at Bimmen/Lobith, whereas nitrate (NO_3) and phosphate (PO_4) concentrations decreased by approximately one third. Accordingly, decadal changes in nutrient elemental ratios shifted the river system from DSi-limitation to P-limitation. Specifically, a seasonal DSi-concentration increase is observed from May to December for the Rhine River (with exception of June). Observed increases in DSi concentration are probably due to improvements in water-basin and land-use management, specifically a reduction in point-source P discharge, leading to P-limiting conditions for diatom growth. Data of the warm season suggest that as the system is moving through the transition from P-excess to P-limitation conditions, P-limitation

according to the elemental ratio DSi/total phosphorus (TP) is occurring later than for the ratio DSi/PO_4-P. Latter ratio will be buffered around $\sim 16{:}1$ during growing season. Reduction of N fertilization is less relevant, as N-limitation with respect to DSi is not achieved, even at the end of the analyzed period, but N-limitation may be reached in the future. Analysis of discharge–DSi relationship supports the hypothesis that DSi increase is affected by increasing P-limitation during the warm period and not only due to hydrological reasons. Results suggest, however, that the influence of hydrological parameters needs to be addressed in research for DSi concentration changes due to changed nutrient loads. Despite an overall increase in water temperature of 3°C over a 50-year period, no correlation with temperature was found for the last two decades of the twentieth century, for which DSi-data were available. In conclusion, in case of eutrophied river systems with excess of P, P-reduction may lead to an increase of DSi concentrations under certain conditions. This in turn is expected to impact not only DSi-sensitive coastal-zone ecosystems impacted by eutrophication but the carbon cycle as well.

Keywords Silica · Trend · Rhine · Nutrient limitation

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Introduction

River damming and eutrophication are reported to be responsible for declining dissolved silica (DSi) concentrations in many fluvial systems (Rahm et al. 1996; Conley et al. 2000; Humborg et al. 2002, 2004, 2006; Friedl et al. 2004). The DSi source in rivers is predominantly the terrestrial land system. A number of factors, including lithology, runoff, gradient of slope, fertilization, and land cover, constitute major controls on the flux of DSi from

terrestrial land into fluvial systems (Bluth and Kump 1994; Semhi et al. 2000a, b; Hartmann et al. 2007, 2010; Beusen et al. 2009; Jansen et al. 2010). During the growing season, DSi concentrations decrease typically stronger in the main branches of river systems than in small tributaries or headwaters. This seasonal pattern occurs as DSi is transferred to amorphous, biogenic silica (BSi), primarily due to the blooming of diatoms (c.f. Admiraal et al. 1990, 1994; Vansteveninck et al. 1992; Fulweiler and Nixon 2005). Typical first-order controls on DSi concentrations in main branches are influenced by ecosystem composition, nitrogen (N) and phosphorus (P) concentrations, flow regime, and light availability (to some part controlled by suspended matter concentration), which influence photosynthesis and respiration rates (e.g., Sferratore et al. 2005). N and P can be limiting factors influencing the rate of transformation from DSi to BSi (Garnier et al. 2006; Billen and Garnier 2007; Billen et al. 2007). Increasing water residence time and flow regulation (due to lakes, reservoirs and weirs, river damming) is responsible for an increase in transformation rates. The sedimentation of "new" BSi in lakes, flood plains, or reservoirs [where it is referred to as the "artificial lake effect" (Humborg et al. 2006)] can remove large proportions of transported DSi. Conley et al. (2000) demonstrate the importance of this effect for Scandinavian catchments where average DSi concentration is inversely related to total lake or reservoir area.

Anthropogenic increase of fluvial nutrient loads often shifts aquatic systems from N- or P-limitation to DSi-limitation (Turner et al. 2003; Garnier et al. 2006; Billen and Garnier 2007). River basins characterized by high N and P loads are primarily located in industrialized countries and or regions dominated by intensive agricultural activity (e.g., Seitzinger et al. 2002, 2005), whereas less populated regions experience lower nutrient loads (e.g., Depetris et al. 2005). High P-concentrations are normally found in river basins with insufficient sewage treatment (point sources) or high contribution of suspended matter P (diffuse) (Garnier et al. 2006). By releasing significant quantities of dissolved inorganic nitrogen (DIN) and P, human activity also influences coastal-zone DSi fluxes. This finding is confirmed by a 1970–1990 Baltic Sea study that used non-parametric time series analysis to identify significant DSi/DIN ratio trends (Rahm et al. 1996). However, in that study, decreasing DSi trends could not be clearly linked to changes in river input or DSi/DIN trends in analyzed river systems. Coastal ecosystems may be significantly affected by decreased DSi fluxes into the coastal zone due to limitations in the growth of diatoms, a major phytoplankton class in the phytoplankton–zooplankton–fish food web (Turner 2002; Kristiansen and Hoell 2002; Harashima et al. 2006; Harashima 2007) and that is replaced by nonsiliceous algae (Billen and Garnier 2007). Diatom abundance

influences also marine carbon burial rates (Buesseler et al. 2007; Harashima 2007). However, atmospheric deposition can also contribute significant amounts of dissolved Si to coastal ecosystems or regional seas, particularly if impacted by anthropogenic emissions, dust storms, or both (Hartmann et al. 2008). The global spatial distribution of river DSi flux is discussed elsewhere (c.f. Dürr et al. 2009; Beusen et al. 2009).

Major temperate rivers typically show highest DSi levels during winter because phytoplankton DSi uptake is lowest in that season (Admiraal et al. 1994; Ietswaart et al. 1999). Thus, an increase in average DSi concentrations of eutrophied rivers should preliminarily be due to increases in DSi during the blooming season. Accordingly, a significant reduction of fluvial N- and P-load may trigger a DSi-concentration increase during the growing season if N- and/or P-limitation is achieved. Garnier et al. (2006) cited limiting elemental ratios for diatoms as 1:1 for DSi/DIN and 1:16 for DSi/total phosphorus (TP). Nevertheless, literature lacks good estimates for the DSi/DIN or DSi/P threshold that must be surpassed to raise DSi concentrations during the growing season for rivers in recovery from anthropogenic syndromes (such as eutrophication) back to their natural stage (c.f. Meybeck 2003). Recent reviews of anthropogenic changes in DSi concentrations and fluxes to coastal zones often focus on diminishing DSi concentrations that are due to damming and eutrophication (e.g., Humborg et al. 2006) but not on DSi increases, which may occur if tributaries contribute higher DSi fluxes that are not consumed by phytoplankton within the river mainstem. Such an increase could be triggered by changes in the controlling factors on weathering or the additional release of DSi by changes in system hydrology, land cover, or the use of fertilizer in agriculture.

Due to improved water management, a reduction in point and general nutrient inputs is observed in many water basins, even though many rivers in the EU still suffer from high N- and P-loads (Mostert 2003; Stalnacke et al. 2003; Meybeck 2004; Hartmann et al. 2006). The EU Water Framework Directive (WFD) (Mostert 2003) stipulates that improved water quality ("good water status") within the EU should be achieved by 2015, and each country should develop national management strategies to achieve the WFD objectives. When legislation becomes effective, either abrupt changes in water quality parameters or transition trends can often be observed (c.f. Hartmann et al. 2006). For some rivers, noticeable water quality improvements were observed in the late 1980s and early 1990s. In Germany, for example, N fertilization was reduced in the late 1980s (Staffel-Schierhoff 2001) and the Rhine Action Plan led to the construction of new sewage treatment plants in the early 1980s. As a result, DIN concentrations have declined since 1990 in the Rhine, whereas the PO_4-P and

TP decline started earlier in the 1980s (Radach and Patsch 2007; Hartmann et al. 2007).

In this study, we tested the hypothesis that a significant reduction in Rhine N- and P-concentrations correlates with increasing DSi concentrations. Specifically, limiting DSi/N and DSi/P molar ratios are included to test whether they function as thresholds. If a reduction in N and/or P in fact triggers a DSi increase, then DSi levels should increase in other regions characterized by decreasing eutrophication. The resulting increased DSi input to coastal zones could then counterbalance the negative effect on DSi caused by the world-wide ongoing construction of reservoirs.

This paper is organized as follows: Details on the Rhine River data are described in "Data", including data analysis techniques (seasonal and trend analysis). Trend and time series analysis results are presented in "Results". Identified trends and implications are discussed in "Discussion", emphasizing the relation between N, P, and Si as well as other analyzed parameters (i.e., temperature and discharge).

Data

The Rhine originates at Lake Toma in Switzerland. It is 1,230-km long and has a catchment of 185,300 km^2 upstream of Bimmen/Lobith, discharging 2,380 $m^3 s^{-1}$. The catchment's hydrology, biogeochemistry, and geochemical baselines have recently been reviewed by Kempe and Krahe (2005) and Hartmann et al. (2007). This study uses data from the Rhine monitoring station Bimmen/Lobith at the German–Dutch border (Fig. 1). The Rhine data were provided by the Federal Institute of Hydrology, Koblenz (BFG) for 1953–2002. Most samples were taken every two weeks, covering temperature, pH, DSi, nitrate (NO_3), nitrite (NO_2), ammonia (NH_3), phosphate (PO_4), chlorine (Cl), sulfate (SO_4), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), dissolved organic carbon (DOC), total organic carbon (TOC), total nitrogen (TN), and TP. Monthly average values of concentrations, pH and temperature were calculated.

Overall and seasonal trends were calculated for each station using the EU-IMPACT project trend analysis software (Libiseller and Grimvall 2002; Stalnacke et al. 2003). Specifically, monotonic (seasonal) trend analysis (nonparametric Mann–Kendall test) was performed on all parameters throughout the observation period. The 2005 version of the trend analysis software was used because of its capability to determine two-sided trend tests. The 5% p-level criterion was selected to identify trend significance. Two time periods were compared for the Rhine River. The first lasted from 1978 to 1989 and is characterized by a decline of TP and PO_4-P concentrations since the early 1980s. The onset of the second period (1990–2001)
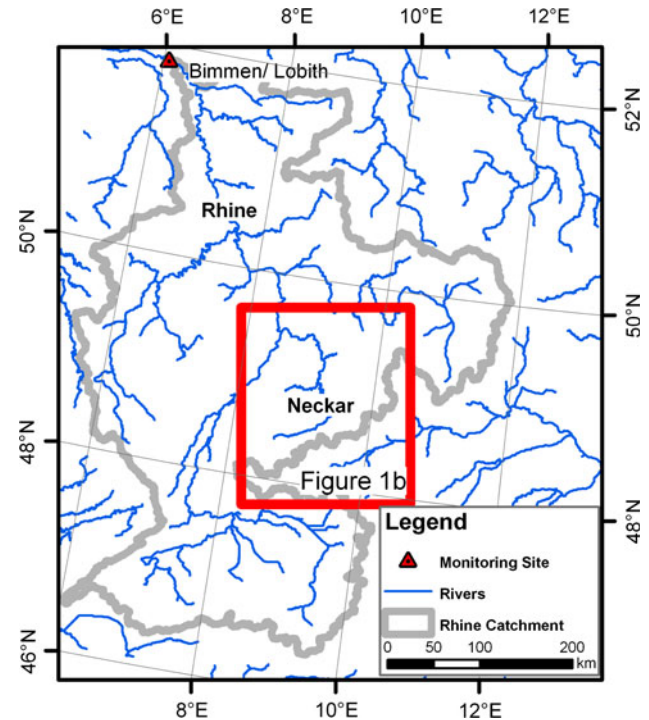

Fig. 1 Location of the monitoring site Bimmen/Lobith for the Rhine River. A comparable analysis was conducted for the Neckar River system with similar results as here shown for the Rhine River [shown in the *rectangle* (**b**)]

coincides with the decline in DIN (dissolved inorganic nitrogen: nitrate plus nitrite plus ammonia) concentrations. With these data, we tested our hypothesis that decreasing N- or P-concentrations correlate with an increase in DSi concentrations with respect to nutrient limitation of diatoms. DSi values, however, are only available from 1978 to 2001 for Bimmen/Lobith.

Results

Nonparametric monotonic trend analysis for monitoring stations and monotonic seasonal trends (Tables 1 and 2) show that nutrient concentrations correlate negatively with DSi concentrations. For the Rhine River, the period with maximum nutrient pollution, from the end of 1978 to 1989 (period 1) is compared with the later period of recovery, from 1990 to 2001 (period 2). These two observation periods allow to evaluate the trends in nutrient concentrations (Hartmann et al. 2007).

Monotonic trends for period 1 and 2

For the Rhine River, a significant trend in DSi concentrations was observed in period 2 (accompanied by a

Table 1 Monotonic trend analysis for all monitoring stations

	DSi			NO_3-N			DSi/DIN			NH_4-N			NO_2-N			PO_4-P			DSi/PO_4-P			DSi/TP			Temperature			pH		
	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p
Rhine/Bimmen 1978–1989	133	*0.1*	0.94	144	*2.2*	0.03*	133	***-0.1***	0.92	144	***-4.7***	0.00*	0		–	144	***-5.6***	0.00*	133	*3.8*	0.00*	514.1	*3.9*	0.00*	144	*1.1*	0.26	144	*4.1*	0.00*
Rhine/Bimmen 1990–2001	144	*4.6*	0.00*	144	***-5.9***	0.00*	144	*10.6*	0.00*	144	***-9.4***	0.00*	126	***-9.8***	0.00*	144	***-3.4***	0.00*	144	*6.8*	0.00*	72	*4.2*	0.00*	144	***0.0***	0.96	144	*2.8*	0.00*

	Cl			SO_4			Ca			Mg			Na			K			DOC			TOC			TP		
	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p
Rhine/Bimmen 1978–1989	144	*1.3*	0.19	144	***-3.0***	0.00*	144	0.7	0.48	144	***-1.1***	0.29	144	0.4	0.70	144	0.4	0.68	127	***-6.2***	0.00*	144	***-5.4***	0.00*	144	***-8.7***	0.00*
Rhine/Bimmen 1990–2001	142	***-9.4***	0.00*	144	***-7.0***	0.00*	144	*1.9*	0.05	71	***-1.9***	0.06	144	***-8.8***	0.00*	144	***-5.5***	0.00*	72	***-6.9***	0.00*	144	***-9.4***	0.00*	72	***-4.7***	0.00*

Chemical definitions can be found in the text

NM nonmissing values, *MK* Mann-Kendall standardized test outcome. *Italics* positive values indicate an increasing trend, ***bold italics*** negative values indicate a decreasing trend

p Significance values of the test statistics

* Significant trends on the *p* level of 5%

decreasing trend in NO_3-N, PO_4-P, and TP concentrations and a significant increasing trend in the DSi/DIN, DSi/PO_4-P and DSi/TP ratios), but a significant DSi trend was not observed in period 1 (although a significant increasing trend in NO_3-N and decreasing trend in PO_4-P and TP were observed). More details are provided in Tables 1 and 2. In both periods, additional decreasing NH_4-N, SO_4, DOC, and TOC trends were observed. In period 2, a decrease in major ions (Cl, Na, and K) was observed, whereas no significant trends were observed in period 1. Ca and Mg trends were not apparent in periods 1 and 2. However, small Ca increases and small Mg decreases were observed (close to the 0.05 *p*-level detection threshold) in period 2. Significant temperature trends were not apparent in either time periods, although a clear increasing trend is detected for the entire available temperature time series (1954–2001) (Table 3). This trend accounts for a temperature increase of approximately 3°C over a 50-year period, and upward seasonal trends for all months except September.

At station Bimmen/Lobith, regression analysis yielded an average DSi-concentration increase of 0.14 mg Si l^{-1} a^{-1} within the 12-year observation of period 2. Annual average concentrations at the beginning of observation period 2 (1990–1992) were 1.5, 3.9, 1.26, 0.1, and 0.26 mg l^{-1} for DSi, NO_3-N, NH_4-N, PO_4-P, and TP, respectively, and 2.6, 2.7, 0.1, and 0.07 mg l^{-1} for DSi, NO_3-N, NH_4-N, and PO_4-P, respectively, at the end of the observation period (1999–2001) and 0.21 mg l^{-1} TP in 1994/1995. This represents a 73% increase in annual DSi concentration and a 31% and 30% decrease in NO_3-N and PO_4-P concentration, respectively (not discharge-weighted). DSi/DIN and DSi/PO_4-P atomic ratio increased from below 0.2–0.5 and 17–41, respectively, at the end of period 2. DSi/TP ratio increased from 7 at the beginning to 13 in 1994/1995. Data for TP were not available at the end of period 2. Time series of nutrient ratios (Fig. 2) revealed a transition period from DSi-limitation to P-limitation from 1995 to 1997, when DSi/PO_4-P ratio was >16 and DSi/TP was <16 during the nongrowing season (autumn to winter). From 1995 to 1998, summer DSi/PO_4-P ratios decreased during the growing season to about 16:1 but were clearly above this ratio from 1999 onward, reaching annual minimal values >30. During period 1, N-limitation with respect to P is given during the growing season and is substituted by P-limitation with respect to N in period 2 (Fig. 3).

Seasonal Rhine analysis

During period 1, a seasonal analysis in January identified a significant upward trend for DSi and a decreasing NO_3-N trend in January and February. However, a significant trend in the DSi/DIN ratio was not observed in period 1 except for the DSi/TP ratio in January/February and the DSi/PO_4-P

Table 2 Seasonal monotonic trend analysis for Bimmen/Lobith, Rhine

Month	DSi			NO$_3$-N			DSi/DIN			PO$_4$-P			DSi/PO$_4$-P			DSi/TP			Discharge		
	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p	NM	MK	p
Bimmen/Lobith (1978–1989)																					
1	11	2.03	**0.04***	12	2.06	**0.04***	11	1.01	0.31	12	−1.51	0.13	11	1.79	0.07	11	2.10	**0.04***	12	−0.41	0.68
2	11	0.95	0.34	12	3.09	**0.00***	11	−0.08	0.94	12	−1.65	0.10	11	1.79	0.07	11	2.26	**0.02***	12	−1.65	0.10
3	11	−0.23	0.81	12	1.65	0.10	11	−0.86	0.39	12	−0.82	0.41	11	0.86	0.39	11	1.32	0.19	12	−0.14	0.89
4	11	0.23	0.82	12	0.41	0.68	11	0.39	0.70	12	−2.06	**0.04***	11	1.32	0.19	11	1.79	0.07	12	0.96	0.34
5	11	−1.56	0.12	12	−1.65	0.10	11	−1.48	0.14	12	−1.92	0.05	11	0.70	0.48	11	−0.23	0.82	12	−0.55	0.58
6	11	0.39	0.70	12	1.23	0.22	11	0.54	0.59	12	−2.19	**0.03***	11	1.63	0.10	11	1.79	0.07	12	0.69	0.49
7	11	0.00	1.00	12	0.27	0.78	11	−0.23	0.82	12	−1.51	0.13	11	0.86	0.39	11	1.01	0.31	12	−1.23	0.22
8	11	−0.86	0.39	12	−0.82	0.41	11	−1.01	0.31	12	−1.65	0.10	11	0.70	0.48	11	0.54	0.59	12	−1.65	0.10
9	11	1.17	0.24	12	0.55	0.58	11	0.86	0.39	12	−1.99	**0.05***	11	2.41	**0.02***	11	2.41	**0.02***	12	0.41	0.68
10	11	0.00	1.00	12	0.69	0.49	11	−0.23	0.82	12	−2.33	**0.02***	11	1.79	0.07	11	2.41	**0.02***	12	−0.27	0.78
11	11	−0.47	0.64	12	1.10	0.27	11	0.08	0.94	12	−1.37	0.17	11	0.86	0.39	11	1.32	0.19	12	−0.41	0.68
12	12	−0.07	0.94	12	1.78	0.07	12	−0.69	0.49	12	−1.23	0.22	12	1.23	0.22	12	1.51	0.13	12	0.00	1.00
Bimmen/Lobith (1990–2001)																					
1	12	0.82	0.41	12	−2.61	**0.01***	12	2.06	**0.04***	12	−1.23	0.22	12	1.37	0.17	6	−0.19	0.85	12	0.41	0.68
2	12	1.44	0.15	12	−1.78	0.07	12	2.74	**0.01***	12	−2.47	**0.01***	12	2.19	**0.03***	6	0.56	0.57	12	1.10	0.27
3	12	0.82	0.41	12	−3.02	**0.00***	12	2.61	**0.01***	12	−1.65	0.10	12	1.51	0.13	6	1.32	0.19	12	1.92	0.05
4	12	1.92	0.05	12	−2.19	**0.03***	12	2.19	**0.03***	12	0.96	0.34	12	1.23	0.22	6	1.32	0.19	12	1.51	0.13
5	12	2.88	**0.00***	12	−2.47	**0.01***	12	3.43	**0.00***	12	−0.69	0.49	12	3.02	**0.00***	6	2.82	**0.00***	12	2.06	**0.04***
6	12	1.65	0.10	12	−3.29	**0.00***	12	3.43	**0.00***	12	−1.51	0.13	12	2.19	**0.03***	6	1.69	0.09	12	0.96	0.34
7	12	2.33	**0.02***	12	−1.10	0.27	12	3.57	**0.00***	12	−0.69	0.49	12	3.29	**0.00***	6	2.82	**0.00***	12	1.23	0.22
8	12	3.37	**0.00***	12	−2.61	**0.01***	12	3.84	**0.00***	12	−0.96	0.34	12	3.57	**0.00***	6	0.94	0.35	12	2.61	**0.01***
9	12	2.47	**0.01***	12	−3.70	**0.00***	12	3.98	**0.00***	12	−0.96	0.34	12	2.47	**0.01***	6	1.69	0.09	12	2.06	**0.04***
10	12	2.06	**0.04***	12	−3.15	**0.00***	12	3.29	**0.00***	12	−2.47	**0.01***	12	2.47	**0.01***	6	1.32	0.19	12	2.06	**0.04***
11	12	2.19	**0.03***	12	−2.88	**0.00***	12	4.25	**0.00***	12	−3.15	**0.00***	12	3.57	**0.00***	6	0.94	0.35	12	−0.27	0.78
12	12	2.27	**0.02***	12	−2.61	**0.01***	12	4.11	**0.00***	12	−2.06	**0.04***	12	2.74	**0.01***	6	0.94	0.35	12	0.69	0.49

Chemical definitions can be found in the text. Both monitoring periods considered are distinguished. Positive values indicate an increasing trend, negative values indicate a decreasing trend. Months with significant DSi trends are marked in italics for comparison

NM nonmissing values, *MK* Mann–Kendall standardized test outcome

p Significance values of the test statistics

* Significant trends on the *p* level of 5%

ratio in September (Table 2). On the other hand, for period 2, DSi concentrations increased from May to December (with the exception of June), whereas DSi/DIN ratios increased over the entire year; DSi/PO$_4$-P ratios increased with the exception of January, March, and April; but DSi/ TP ratios increased only during May and July (TP data are available only until the end of 1995). July was the only month that did not exhibit a significant trend decrease for NO$_3$-N. DSi/DIN ratios increased at Bimmen/Lobith for all months in period 2. Finally, we compared seasonal patterns that occured at the beginning of the recovery period to those occurring at the end of the analyzed period (Fig. 4). In 2001, the local maxima previously found in the summer DSi concentration were no longer visible. DSi-limitation vanished from April/May on and was substituted by P-limitation with respect to PO$_4$-P. In spring 2001, when no DSi-limitation was found during spring, DSi/PO$_4$-P ratio

was decoupled from seasonal trend of DSi concentration if compared with previous years (Fig. 4).

Influence of hydrology

A strong correlation between DSi-and NO$_3$-N fluxes and monthly mean river discharge was observed (Fig. 5), and PO$_4$-P fluxes correlated less strongly. Besides the increasing DSi trends, observed DSi flux trends may in part be due to 1999–2001 Rhine River discharges. A significant negative trend for discharge was detected in period 1 ($p \sim 0.049$) and a highly significant positive trend in period 2 ($p < 0.001$). The Rhine had an average discharge of 2,524 m^3 s^{-1} in period 1 and 2,258 m^3 s^{-1} in period 2, and discharges during the warm season (April–September) were 2,436 and 1,983 m^3 s^{-1}, respectively. Seasonal trend analysis is displayed in Table 2, indicating no better

Table 3 Seasonal trend statistics of temperature for Bimmen/Lobith using monthly average temperature data from 1954 to 2001

Temperature °C			
Month	NM	MK	p
1	48	3.30	**0.00***
2	47	2.71	**0.01***
3	48	3.25	**0.00***
4	48	2.49	**0.01***
5	48	2.42	**0.02***
6	48	2.72	**0.01***
7	48	2.79	**0.01***
8	48	4.19	**0.00***
9	48	0.96	0.34
10	48	2.14	**0.03***
11	48	3.06	**0.00***
12	48	2.43	**0.02***

NM nonmissing values, *MK* Mann–Kendall standardized test outcome (positive values indicate an increasing trend)

p Significance values of the test statistics

* Significant trends on the *p* level of 5%

explanation for DSi trends than observed nutrient limitation. To discard a possible discharge effect, the Rhine DSi discharge relationship was analyzed for all four seasons (Fig. 6). Data sets were separated into a first and second period for this, considering change points according to P-limitation. Discharge DSi pattern analysis revealed increasing DSi concentration with increasing discharge (Fig. 6). However, the second period, characterized by P-limitation in the growing season, showed increased DSi concentrations with respect to the corresponding discharge. Discharge influences as a biasing factor for the nutrient limitation hypothesis on observed DSi trends in the main stems were thus discarded.

Discussion

The main branch data of the Rhine show that nutrient ratios were significantly shifting over at least the last decade of the twentieth century. Trend analysis confirms that a decrease in DIN, PO_4-P, and TP (likely resulting from increased sewage treatment and changes in agriculture) is accompanied by an increase in DSi concentrations. The origin of the "additional" DSi probably is a lower consumption of DSi (e.g., by diatoms) due to decreased nutrient availability. This is evidenced by increasing minimum DSi concentrations during the growing season (Figs. 2–6). In the Rhine River, maximal phytoplankton growth rates occur in spring (Weitere et al. 2005), and algae growth is mainly controlled by light availability
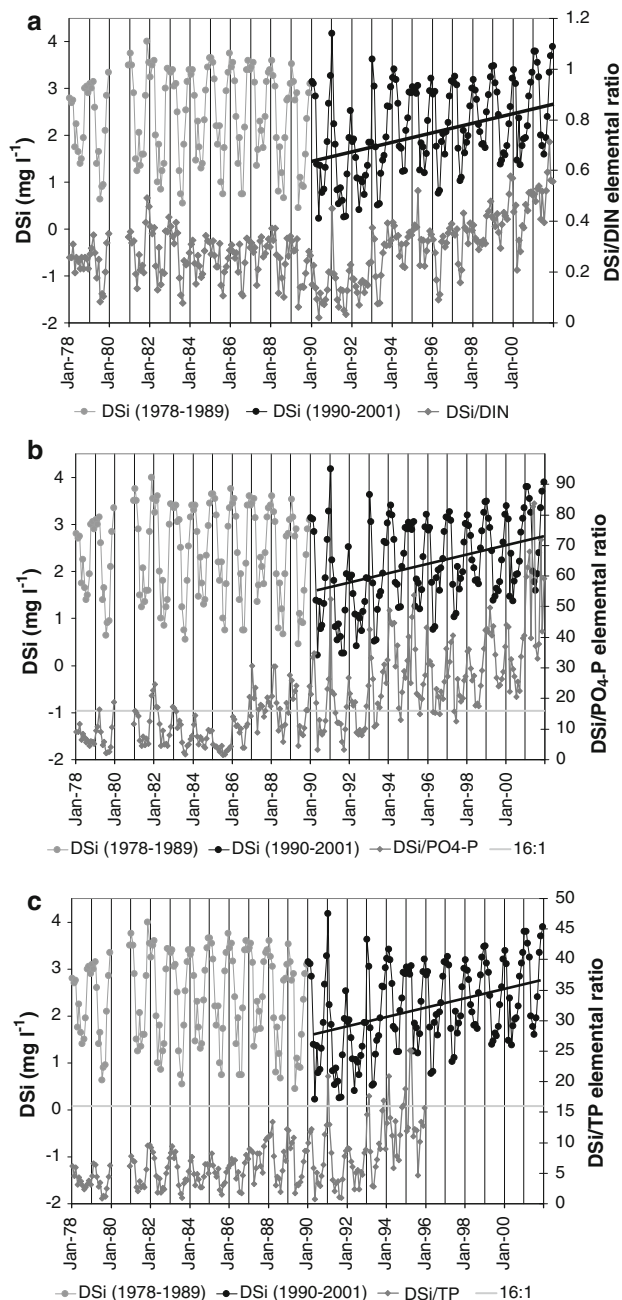

Fig. 2 Monthly concentrations of DSi (in mg Si l^{-1}) and DSi/DIN (**a**), DSi/PO_4-P (**b**), and DSi/TP (**c**) elemental ratios (DIN constitutes the sum of nitrate, nitrite, and ammonia) for the station Bimmen/Lobith, Rhine River (Fig. 1). The increasing trend based on regression analysis in DSi concentrations since 1990 for Bimmen/Lobith is displayed

(Ietswaart et al. 1999). Diatoms are responsible for >80% of algal biomass at the Bimmen/Lobith station (Schol et al. 2002) and in the Lower Rhine (Weitere et al. 2005). Bacteria, flagellates, ciliates, and rotifers contribute only minor proportions to the algal biomass. However, benthic organisms are important for recycling BSi in the Rhine River (Vansteveninck et al. 1992; Schol et al. 2002;
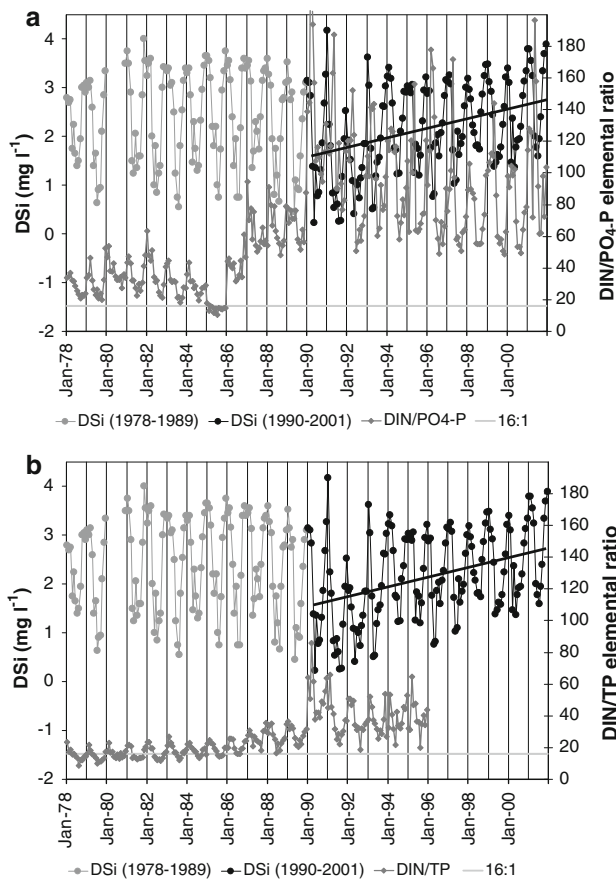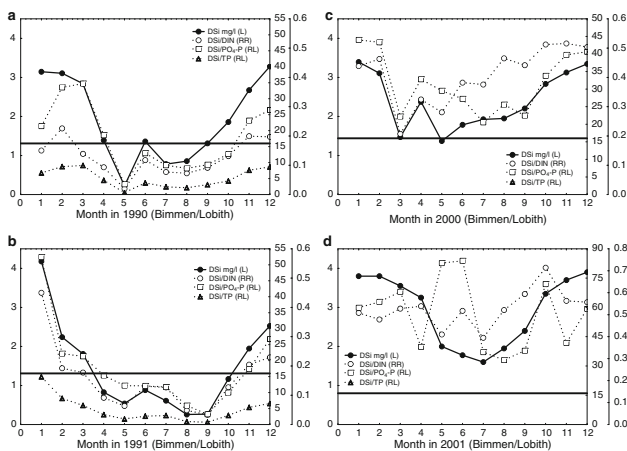
Fig. 3 Monthly concentrations of DSi (in mg Si l^{-1}), and DIN/PO$_4$-P (**a**) and DIN/TP (**b**) elemental ratios (DIN constitutes the sum of nitrate, nitrite and ammonia) for the station Bimmen/Lobith, Rhine River (Fig. 1). The increasing trend based on regression analysis in DSi concentrations since 1990 for Bimmen/Lobith is displayed

Fig. 4 Seasonality in DSi (mg Si l^{-1}), DSi/DIN, DSi/PO$_4$-P, and DSi/TP elemental ratios for station Bimmen/Lobith (1990, 1991, 2000, and 2001). *L* left axis, *RL* left axis on the right, *RR* right axis on the right

Sferratore et al. 2005), but the impact of these organisms could not be determined in this study. Ecosystem functioning (Admiraal et al. 1994; Schol et al. 2002) is likely responsible for a small summer peak in DSi concentrations (indicated by a second decline of DSi).

Nutrient limitation

Levels of nutrient fluxes into the river systems declined due to a reduction in the application of fertilizers in agriculture (Staffel-Schierhoff 2001) and due to improved sewage treatment (detailed nutrient time series analysis are provided in Hartmann et al. 2007). Overall trends in DSi/PO$_4$-P and DSi/TP atomic ratio suggest that a transition from DSi-limitation to P-limitation occurs during the warm season (i.e., DSi/PO$_4$-P >16) and is related to the observed DSi warm-season trend. N-limitation is excluded as a possible influence on observed DSi trends because DIN is present in excess with respect to plankton-available-P since the 1990s, and at the outlet of the studied catchment, no N-limitation with respect to DSi could be observed. This nutrient limitation interpretation is in accordance with studies of other river systems (Billen and Garnier 2007). Thus, the seasonal nutrient concentration analysis supports the hypothesis that decreasing P-concentrations affect the river's internal Si cycle. This observation may hold for other, larger, catchments with a similar flow regime if a comparable nutrient reduction occurs, resulting in a shift from DSi- to P- or N-limitation conditions.

In period 1 (1978–1989), average DSi with 2.4 mg Si l^{-1} is higher than observed in the minimum year 1990 for the Rhine (when DIN started to decrease). Comparison of DIN/PO$_4$-P and DIN/TP ratios with DSi concentrations in this period reveals that during the growing season, DSi concentration stops decreasing when N-limitation with respect to P (DIN/PO$_4$-P $\sim$16) occurs and the annual minima of DIN/TP is reached (c.f. Billen and Garnier 2007; Garnier et al. 2007; Billen et al. 2007; Garnier and Billen 2007). Period 2 is characterized by P-limitation with respect to N and DSi. This finding emphasizes the observation that limiting nutrient ratios have impacted DSi concentrations and thus DSi fluxes in both periods for the Rhine River. The coincidence of decreasing DSi concentrations with DSi/PO$_4$-P ratios >16 can only be explained if P is available for consumption. Probably, mobilization of PO$_4$-P from suspended matter (organic and inorganic) is an additional important P source during the growing season in the transition period from DSi-limitation during peak plankton growth to P-limitation (for both PO$_4$-P and TP) (c.f. Clasen et al. 1982; Conley et al. 1995). In general, three further sources of P, besides dissolved PO$_4$-P, are known: first, mineralization of biomass due to respiration processes; second, mobilization of P and subsequent uptake
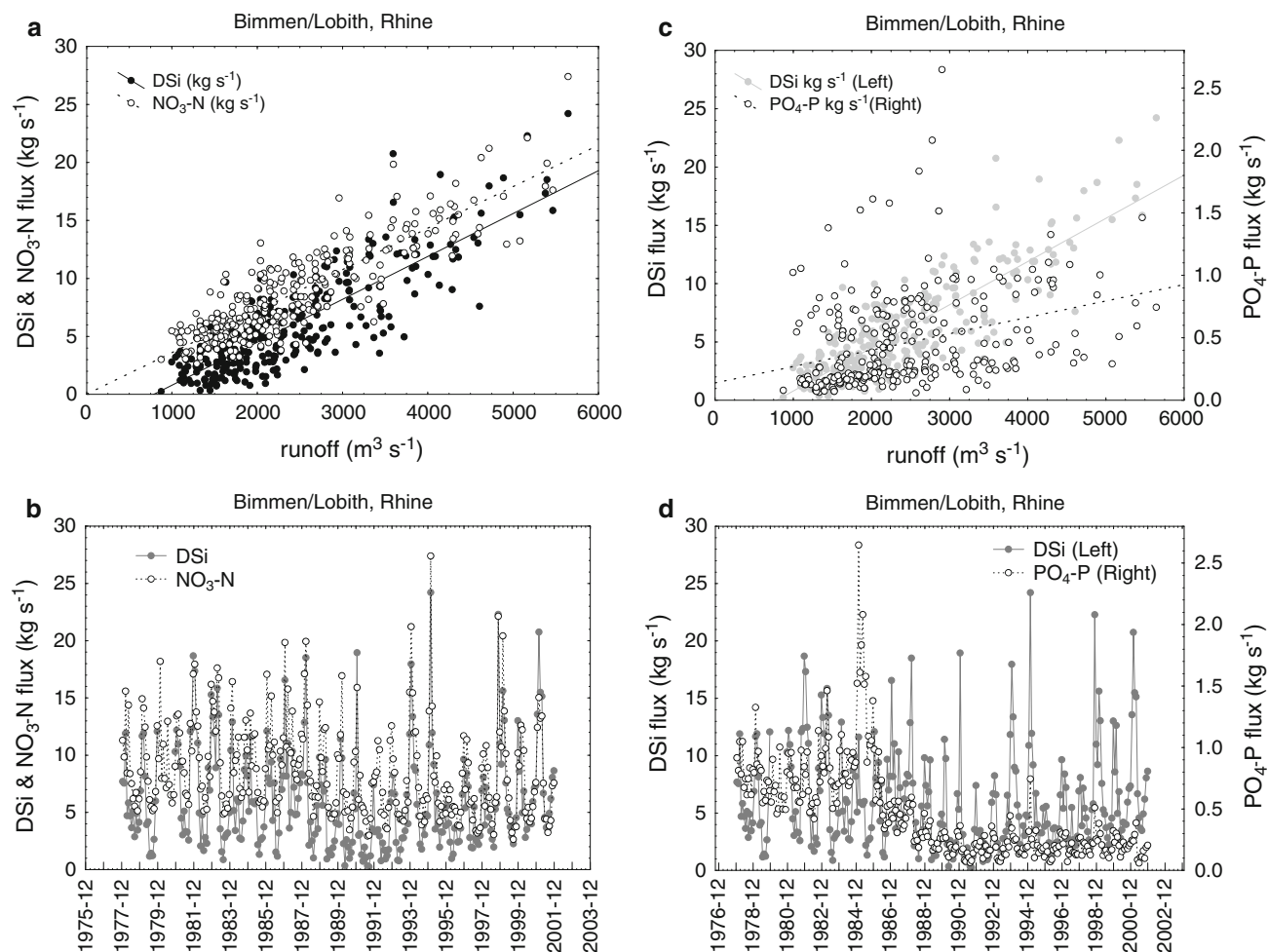
Fig. 5 Relationship between discharge and DSi- and nitrate-N-, and PO₄-P fluxes for Bimmen/Lobith. Note that variability in DSi fluxes is much larger than variability in concentrations

from suspended matter; and third, organic dissolved P (for which no data are available). TP represents here both DP and PP (particulate P).

Runoff effect

Besides nutrient limitation, discharge variation constitutes an important variable in this analysis, since DSi, N, and P-concentration variability was less than flux variability, and a positive correlation between DSi flux and discharge exists for both systems (compare Figs. 2, 5, and 6). It follows that: (1) nutrient fluxes are highly sensitive to discharge, and (2) the hydrological regime is another important factor influencing the seasonal growth rate of diatoms. This is because light availability is in part controlled by hydrology due to its influence on suspended matter concentration and thus light intensity in the water column (Ietswaart et al. 1999). Accordingly, results show that a logarithmic relationship exists between DSi concentrations and discharge in each season. The strong observed increase in DSi concentration in

period 2 can thus to some extent be attributed to low summer discharge at the beginning of this period, particularly in the month May and in the period from August to October (Table 3), as indicated by comparison of DSi concentrations with DSi fluxes (Fig. 6). In contrast to period 2, period 1 is characterized by higher discharge values on average, specifically during the warm season. However, the first half of period 2 is characterized in general by lower DSi concentrations with respect to discharge than the second half (specifically during the summer season when DSi uptake by diatoms is high and P-limitation is present). Thus, discharge may have been contributing in part to calculated average increases in DSi concentration of ∼70% throughout period 2, but the nutrient limitation hypothesis still holds. In addition, it is concluded that comparably high average DSi in period 1 if compared to period 2 was in part due to the observed discharge effect on ecosystem functioning impacting DSi concentrations.

Even though discharge influences concentrations to some extent, the hypothesis "DSi increases are due to
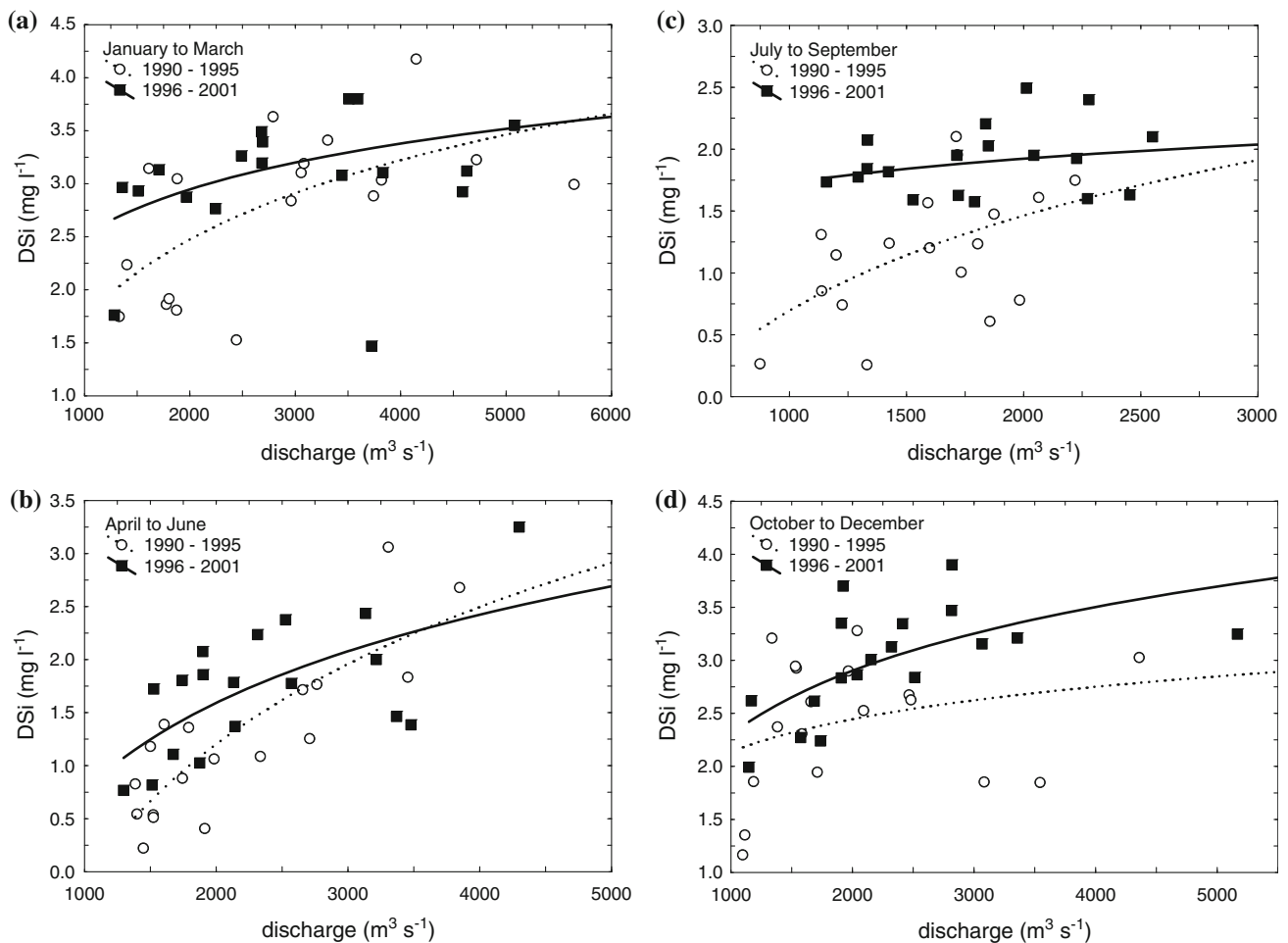
Fig. 6 Comparison of the discharge—DSi relationship at Bimmen/Lobith for the four seasons. First and second half of period 2 are compared, and for better visibility, the log-regression function of each

subsample is plotted (best fit). For winter, one observation from period 2 was discarded for calculating best fit regression, as it falls out of range for the winter distribution pattern (discharge/DSi: 3,700/1.5)

nutrient limitation" is not rejected. Differences in flux patterns, nutrient concentrations and elemental ratios were clearly characterized by seasonality at all times. It is concluded from this observation and from presented results that analysis of concentrations instead of flux values (due its large variability and dependence on discharge) is appropriate. In addition, alternating wet and dry years influence DSi fluxes (Fig. 5). This is because extreme hydrological events (in dry and wet years) affect DSi, N, and P fluxes more than concentrations alone. As average annual DSi concentrations increase, effects on both coastal and estuarine ecosystems (including the Rhine delta) are possible. This is because DSi availability has a pronounced impact on coastal-zone ecosystem structures (Harashima et al. 2006; Harashima 2007).

Further effects

At the beginning of period 2, very low DSi values (close to the detection limit) were observed in May. Those low DSi
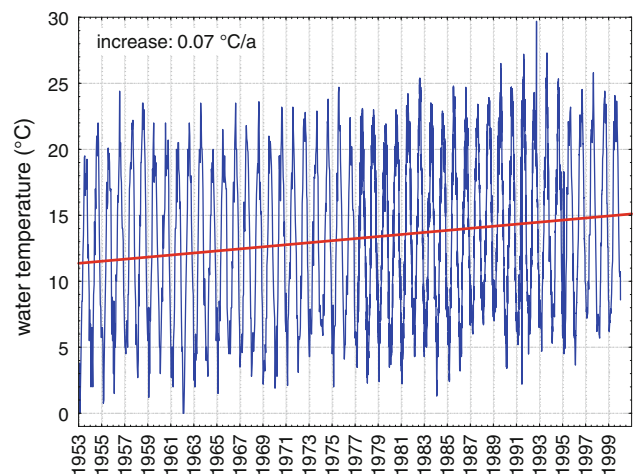

Fig. 7 Water temperature at Bimmen/Lobith station increased by 0.07°C per year. The *line* indicates the linear regression trend

values were accompanied by a following breakdown of diatom population in June (c.f. Admiraal et al. 1994; Schol et al. 2002), evidenced by an increase in DSi. Because of

these breakdowns in diatom population, no positive trend for June was detected for the Rhine River. The discovered trends in autumn can be linked with increases in the elemental nutrient ratio DSi/PO$_4$-P. Temperature changes are excluded in this analysis as a major factor influencing possible diatom growth changes, since the 1990–2001 temperature did not change significantly in either river system. However, a significant increase in the Rhine River temperature over a period of five decades was observed ($\sim$3°C; Fig. 7), which may have impacted ecosystem functioning. Sewage plant DSi contributions can likely be rejected, as their estimated overall contribution was <2% of the total DSi input into the rivers (Van Dokkum et al. 2004).

Conclusion

It is suggested that the observed increase in DSi concentrations is primarily due to improvements in water basin and land use management (i.e., a reduction in the application of N fertilizer and improved sewage water treatment). It was shown that decreasing PO$_4$-P concentrations were likely responsible. It appears that instream bioactivity (due to photosynthesis and decay of diatoms) affects annual mean DSi concentrations to a greater extent than discharge. At Bimmen/Lobith, a seasonal increase was observed from spring to autumn.

Increasing DSi concentration, due to less uptake by diatoms, results in a decreasing BSi proportion of transported silica. This should result in higher export of silica from the river system (in case of constant discharge), because it can be assumed that on average, less BSi is retained, e.g., due to sedimentation in flood plains (Admiraal et al. 1990). Specifically, during warm periods, DSi export from the system would thus increase. However, it remains difficult to assess the amount of BSi retained. It can be assumed that in cold seasons, silica export changes little due to changes in nutrient ratios, because of low photosynthesis rates and highest DSi concentrations. It could be argued that the theoretical BSi content in the river water should be equivalent to the reduction of DSi concentration from high winter concentrations. However, DSi flux during the cold period dominates due to normally high discharge during the winter period and low discharge in the summer season, often reaching its minimum in September. In addition, it should be considered that during warm (and dry) periods, DSi in waters from the terrestrial system may increase due to an increased groundwater proportion from headwaters.

The study of DSi trends will become increasingly important in light of recent EU efforts to improve water quality throughout much of Europe within the EU Water Framework Directive. A significant reduction in river N and P-concentrations, resulting in N- or P-limitation, is expected to increase DSi fluxes to the coastal zone, thereby impacting those coastal-zone ecosystems that are sensitive to DSi river input and hence also to regional carbon cycles.

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