Biogeochemistry (2011) 106:475–487
DOI 10.1007/s10533-010-9527-1

A trade-off between dissolved and amorphous silica transport during peak flow events (Scheldt river basin, Belgium): impacts of precipitation intensity on terrestrial Si dynamics in strongly cultivated catchments

Adriaan Smis · Stefan Van Damme · Eric Struyf · Wim Clymans · Bas Van Wesemael · Elisabeth Frot · Floor Vandevenne · Thomas Van Hoestenberghe · Gerard Govers · Patrick Meire

Received: 3 November 2009 / Accepted: 3 September 2010 / Published online: 21 September 2010

Abstract Amorphous, biogenic Si (ASi) is stored in large amounts in terrestrial ecosystems. The study of terrestrial ASi mobilization remains in the pioneer research stage: most Si budget studies have not included the biogenic amorphous Si stock and fluxes. This hampers our ability to accurately quantify terrestrial mobilization of Si, which is—through ocean carbon burial and CO_2 uptake during terrestrial Si weathering—intricately linked to global carbon budgets. We studied detailed concentration and load patterns of dissolved (DSi) and ASi during several high-discharge events in eight first-order river basins. Based on high frequency discharge measurements and concurrent analysis of ASi and DSi concentrations at base flow and during intense precipitation events, we were able to attribute a percentage of yearly ASi and DSi fluxes to both base flow and precipitation event related surface run-off. Our results show ASi and DSi concentrations in upstream river basins to be intricately linked to each other and to discharge, and ASi transport constitutes an important part to the total transport of Si even through first-order river basins (up to 40%). Based on our observations, increased occurrence of peak-discharge events with global climatic changes, and lowered importance of base flow, will coincide with drastic changes in ASi and DSi dynamics in the river continuum. Our work clearly shows ASi dynamics should be incorporated in global Si budgets now, even in low-order small river basins.

A. Smis · S. Van Damme · E. Struyf (✉) · F. Vandevenne · P. Meire
Department of Biology, Ecosystem Management Research Group, University of Antwerp, Universiteitsplein 1C, 2610 Wilrijk, Antwerp, Belgium
e-mail: eric.struyf@ua.ac.be

W. Clymans · G. Govers
Department of Geology, Physical and Regional Geography Research Group, Catholic University of Leuven, Celestijnenlaan 200 E, 3001 Heverlee, Belgium

B. Van Wesemael · E. Frot
Georges Lemaître Centre for Earth and Climate Research, Earth and Life Institute, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

T. Van Hoestenberghe
Flemish Environment Agency, Sluizenweg 2, 9050 Gentbrugge, Belgium

T. Van Hoestenberghe
Soresma, Poortakkerstraat 41, 9051 Ghent, Belgium

Keywords Amorphous silica · Rain events · Suspended matter · Erosion · Global silica cycle · Land use · Precipitation intensity

Introduction

Diatoms are the most efficient oceanic carbon sink (Dugdale et al. 1995). Diatoms deplete oceanic dissolved Si (DSi) concentrations to a concentration near biological limitation (5 μM). After diatoms decay, the biogenic or amorphous silica (ASi) in the diatom frustules sinks into the deeps. Yet, 97% of the settling ASi is recycled to DSi before it can reach the ocean floor: as such, the diatom community is nearly perfect at sustaining its own need for DSi (Tréguer et al. 1995). Still, without replenishment of the remaining 3% from terrestrial Si mobilization, diatom production in the ocean could gradually decline, with devastating effects on oceanic primary production and associated carbon burial (Rabosky and Sorhannus 2009). Any shift from siliceous (diatoms) to non-siliceous phytoplankton decreases the net sequestration of CO_2 and consequently the flux of CO_2 from the atmosphere towards the ocean floor (Tréguer and Pondaven 2000). Therefore, the biological carbon pump is often referred as the "biological Si pump" (Dugdale et al. 1995; Ragueneau et al. 2000).

The Tréguer et al. (1995) global ocean Si budget study included only DSi export from the terrestrial environment: ASi transport through rivers was considered insignificant compared to DSi fluxes. However, later studies have clearly shown that ASi transport from the continents constitutes a substantial part of Si fluxes into the ocean (e.g. Conley 1997). The percentage of the total flux attributed to ASi as estimated by Conley (1997)—16%—was a conservative estimate, as it was based on a limited number of samples from a limited number of rivers: the study of terrestrial ASi mobilization remains in the pioneer research stage (Conley et al. 2008). Dürr et al. (2009) suggested estimating total particulate silica transport based on suspended matter concentrations. However, this does not provide an accurate quantification of the reactive Si fluxes. The mineral Si part can be considered inert at shorter biological timescales (Van Cappellen 2003).

A lack of knowledge limits our ability to quantify the importance of ASi transport in global and local Si budgets, and our ability to link it to changes in land use and climate. ASi is stored in large amounts in terrestrial ecosystems (Conley 2002), like wetlands (Struyf and Conley 2009), forests (Gérard et al. 2008) and grasslands (Blecker et al. 2006). The ASi is located both in biomass and soils, and is a diverse collection of plant phytoliths, diatoms and testate amoebae and a variety of amorphous mineral compounds (Clarke 2003). Delivery of ASi from the land surface to river systems is expected to occur mainly during short high-intensity precipitation events as the latter lead to peak runoff rates, inducing soil erosion and mobilizing suspended matter (Fabres et al. 2008; Gouze et al. 2008). The frequency of intense precipitation events is expected to rise significantly in large parts of the world (Trenberth et al. 2003). ASi mobilization from soils is also potentially strongly linked to land use changes, which directly control the erosion processes that are at the basis of suspended matter transport (Woodward and Foster 1997). However, the study of the relative dynamics of ASi and DSi during peak discharge events remained up till now hypothetical. In recent modelling studies (Thieu et al. 2009), DSi concentrations are still considered to be identical in both base flow and surface run-off, and ASi concentrations in suspended matter (SPM) are considered constant during such peak flow events.

While ASi loads can undergo significant changes during transport through the aquatic continuum due to deposition in wetlands (Struyf et al. 2007a) or lakes (Humborg et al. 1997), due to dissolution to DSi or to uptake of DSi into vegetation (Struyf et al. 2007b) or diatoms (Conley et al. 1993), quantification of basic ASi mobilization at the scale of small upstream river catchments forms a necessary key input for models of terrestrial–aquatic exchange of Si. Low order river catchments (1–3) drain over 90% of the land on a global scale (Vorosmarty et al. 2000). In this paper, we studied detailed concentration and load patterns of both DSi and ASi during several high-discharge events in eight first-order river basins. All basins were located in the Belgian loess belt. This region is characterized by a hilly topography and silty loamy top soils and is mainly used as arable land. The combination of these three characteristics makes the region highly susceptible to soil erosion. Based on high frequency discharge measurements and concurrent analysis of ASi and DSi concentrations at base flow and during intense precipitation events, we were able to attribute a percentage of yearly ASi and DSi fluxes to both base flow and precipitation event related surface run-off. Our results show ASi and DSi concentrations in upstream river basins are intricately linked to each other and to discharge, and ASi transport constitutes an important part to the total transport of Si even through first-order river basins.

Materials and methods

Study area

The study was performed in the Flemish (Northern Belgium) part of the river Scheldt basin (Fig. 1). This area has a hilly topography in the south (with a maximal elevation of 157 m) while the northern part is almost flat. The area is one of the most industrialized and populated regions in Europe (population density $\sim$447 inhabitants per km^2). The entire study area has a temperate climate with a long-term (1971–2000) mean annual precipitation of 820 mm and a mean January and July temperature of respectively 3.1 and 17.7°C. Although the total precipitation is spread equally throughout the year, intensity, duration and frequency of precipitation vary throughout the year. In summer, storms are shorter but more intensive, whereas winter storms are generally less intensive but more frequent.

Eight stream catchments where arable land use is highly dominant were selected (Fig. 1; Table 1). The catchments are situated in the southern part of Flanders and are part of two larger sub-basins: the Demer basin (four catchments with sample stations at Muizen, Velm, Piringen and Wellen) and the Bovenschelde basin (four catchments with sampling stations at Etikhove, Leupegem, Maarke Kerkem and Broekbeek). Both basins belong to the most erosion-sensitive area in Flanders and are therefore monitored by the Flemish Environment Agency (VMM). Monitoring consists of continuous precipitation and discharge measurements as well as sampling for suspended matter (SPM) concentration during peak flow events. The population density in these two regions ($\sim$137–276 inh/km^2) is low compared with the average of Flanders: all sampled catchments are dominated by cropland (Table 1).

Sample collection

Samples from the eight small scale catchments were collected by auto-samplers of the Flemish Environmental Agency (VMM) during peak discharge events. Peak event auto-sampling started when discharge in the rivers was twice the modal base flow discharge

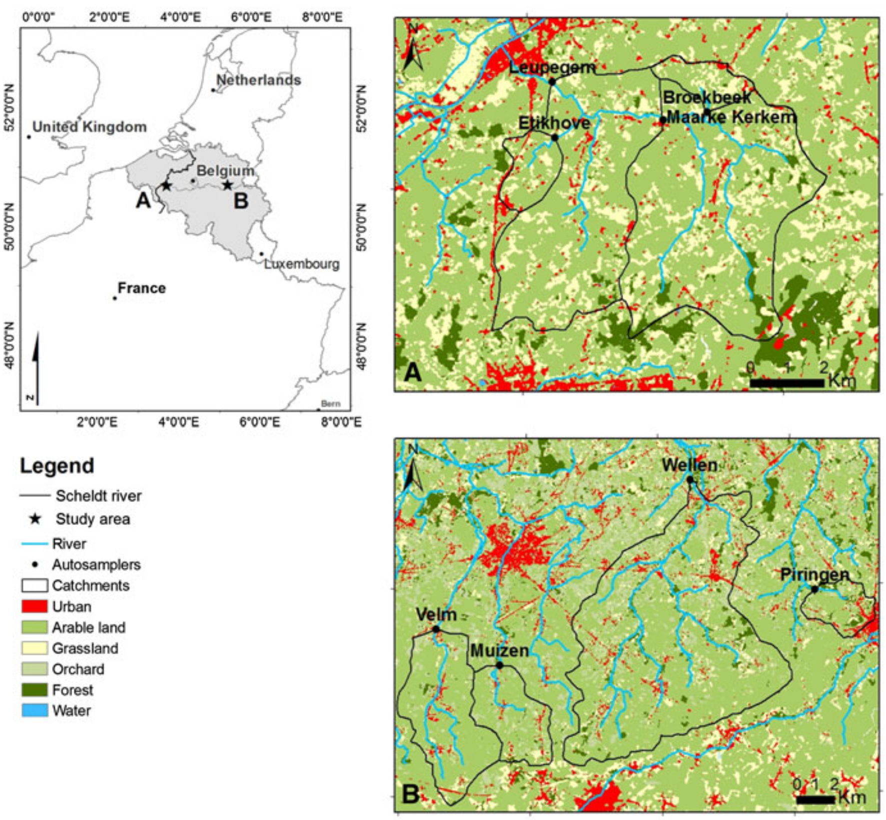

Fig. 1 Map of the location of and land use in the sampled watersheds

Table 1 Characteristics of the eight catchments

Catchment	Mean base flow concentration		n (base flow)	n (peak flow)		Q_m (m^3/s)	Area (km^2)	Land use			
	DSi (10^{-6} M)	ASi (10^{-6} M)	DSi and ASi	DSi	ASi			Cropland (%)	Grassland (%)	Forest (%)	Urban (%)
Leupegem	457	6.24	3	51	38	0.104	50.3	70.4	20.7	3.3	2.8
Maarke Kerkem	452	6.30	3	30	19	0.050	28.0	66.9	21.0	4.8	2.5
Broekbeek	429	8.87	14	51	25	0.024	2.2	67.0	26.6	0.7	5.7
Etikhove	432	3.36	3	14	10	0.010	2.6	74.2	18.7	0.3	6.9
Velm	500	4.35	4	57	51	0.082	29.5	89.4	3.4	1.3	3.4
Muizen	407	9.10	3	156	124	0.012	15.7	82.9	4.0	1.5	3.1
Wellen	323	5.78	3	31	31	0.244	107.6	82.1	5.5	4.6	3.2
Piringen	233	6.06	3	42	32	0.030	8.2	74.3	6.1	10.3	9.1

Land use, area, modal discharge (Q_m) (2006–2008), the number of peak flow samples (n) analyzed for ASi and DSi, number of base flow samples analysed for ASi and DSi (n) and mean ASi and DSi concentrations (μM) observed at base flow

(Table 1). Samples were taken near the bottom of a concrete flume (ca. 20 cm from the flume bottom). Samples were stored dark and cool (2–3°C) after collection from the auto sampler. From each sample two subsamples, one for DSi and ASi and one for SPM were taken. For three catchments (Leupegem, Muizen, Etikhove), total organic carbon (TOC) was also determined. Additionally, to complete the data-set, catchments were sampled manually three times at base flow conditions (September 2008, October 2008, March 2009).

In total, 432 DSi and 330 ASi samples were taken at peak flow, ranging from 17 to 159 samples per catchment (Table 1), irregularly spread over the period from February 2007 until March 2009. Available discharges are averages over 15 min time intervals. Modal base flow discharge of each stream was calculated as the mean of the five discharges with highest probability density during the period 2006–2008.

Base flow separation

In order to make an objective and structural separation between base flow periods and peak flow events in the calculations of annual transported Si loads (see further), the contribution of base flow to total flow was calculated by using the base flow separation method WETSPRO (Water Engineering Time Series PROcessing tool; Willems 2009). In case base flow discharge was modelled higher than observed total discharge, base flow discharge was considered the total discharge. In addition, WETSPRO was used to select clear base flow periods in which base flow samples were taken.

Analysis

For DSi analysis, about 10 ml was filtered (Chromafil® A-45/25, pore size 0.45 μm) from the water samples. The filtrate was analysed spectrophotometrically for DSi concentration on a Thermo IRIS (Inductively Coupled Plasma Spectrophotometer; Iris®, detection limit 0.009 ppm Si).

ASi-concentrations were measured using the wet chemical digestion method in hot alkali (Conley and Schelske 2001). Depending on the SPM concentration, 5–25 ml was filtered from the well-mixed water sample on a 0.45 μm filter and air-dried at 20°C. ASi was extracted from the filters in a 0.1 M Na_2CO_3 solution at 80°C in a shaking hot water bath for 1 h. 10 ml of the extract was then filtered (Chromafil® A-45/25, pore size of 0.45 μm). Blank extractions were subtracted to account for DSi release from recipients and chemicals.

A correction for the simultaneous dissolution of mineral silicates was applied. This correction was implemented through execution of time course extractions (Conley and Schelske 2001). The fact that most ASi dissolves completely within 1 h of digestion in hot alkali allows determining the interference of mineral silicates during the extraction. Only about 20% of the samples were sequentially extracted, i.e. additional analysis of the extract after 2 and 3 h. For each sequentially extracted sample, the slope of the linear relation between extracted DSi and extraction time was determined. We found a significant linear relation ($R^2 = 0.283; p < 0.0001$) between the extraction slopes and the measured ASi-concentration of the first sequential sample (after 1 h). The slope derived from this linear relationship was assumed to correct for mineral dissolution in both sequentially and non-sequentially extracted samples. SPM in all sampled catchments is characterized by similar lithology, and the mineral slope will mainly be dependent on SPM concentration (which also determines ASi-concentrations per water volume).

SPM was determined gravimetrically after filtration on precombusted Whatman 42 filters (pore size of 2.5 μm).

TOC was analysed using the Walkley–Black procedure, a rapid dichromate oxidation method of organic matter (Walkley and Black 1934).

Annual load calculations

Observed relationships between discharge and silica (ASi and DSi) concentrations (see "Results" section) were used to predict year-long time series of ASi and DSi concentrations in 2007 based on 15-min average discharges in all catchments. Relationships between discharge and Si concentrations were explored using simple linear regression analysis. Si variables were $\log_e$ transformed in case of non normality, and comparison between linear (linear x-axis) and logarithmic (logarithmic x-axis) correlations was performed by using the Akaike's Information Criterion (AIC). Different relations were distinguished for periods of base and peak flow. The ratio (r) of base flow discharge, modelled by using WETSPRO (Willems 2009), to measured total discharge was used as criterion to differentiate between peak and base flow periods. However, as modelled base flow discharge could not exactly follow the small fluctuations of measured discharge during base flow periods (no significant precipitation and no increase in discharge), this ratio was chosen lower than 1. All calculations were repeated for three ratios (e.g. 0.7, 075 and 0.8) to test the sensitivity of the results for this parameter. The ratios were selected based on inspection of the ratio during clear base flow periods. A linear relation fitted (DSi and ASi concentrations versus discharge) to the base flow sampling measurements and the autosampler measurements at the lowest discharges was used to predict base flow ASi and DSi concentrations in a similar way as during the peak events. Finally, total transported Si was calculated as summation of the product of concentration and discharge over each period of 15 min (Eq. 1) with $[\mathrm{Si}]_i$, the Si concentration during time interval i, Q_i, the discharge during time interval i, and n, the number of time intervals of 15 min present in 1 year.

$$\text{Si-load} = 900\ \mathrm{s} \sum_{i=1}^{n} [\mathrm{Si}]_i . Q_i \qquad (1)$$

Results

Discharge

Discharge data at the eight locations were available from 2006 to 2008 (VMM, 2006–2008). Discharges of all catchments were characterized by a strongly skewed distribution resulting from the fast re-establishment of base flow conditions after peak flow events (Fig. 2). Based on discharge data of 3 years (2006–2008), modal base flow discharges varied between 0.012 and 0.244 m^3/s (Table 1). The maximal discharges during the sampled peak flow events are indicated on the general discharge frequency distribution for the catchments of Muizen and Leupegem (Fig. 2).

DSi and ASi concentrations

Discharge weighted (based on relative occurrence frequency of the discharge at sampling during 2006–2008) mean DSi concentrations differed between the different catchments (Table 1). Observed DSi concentrations ranged from lowest values at Piringen (230 μM) and Wellen (320 μM) to highest values of 450–500 μM at Velm, Leupegem and Maarke Kerkem. ASi concentrations observed under base flow conditions were always low and varied between 6 and 23 μM (Table 1).

The relationship between DSi as well as ASi concentrations and discharge was assessed using linear regression statistics. Due to non normality, DSi and ASi concentrations were $\log_e$ transformed for most streams before executing regression analysis. Generally, DSi concentrations decreased and ASi concentrations increased with increasing discharge

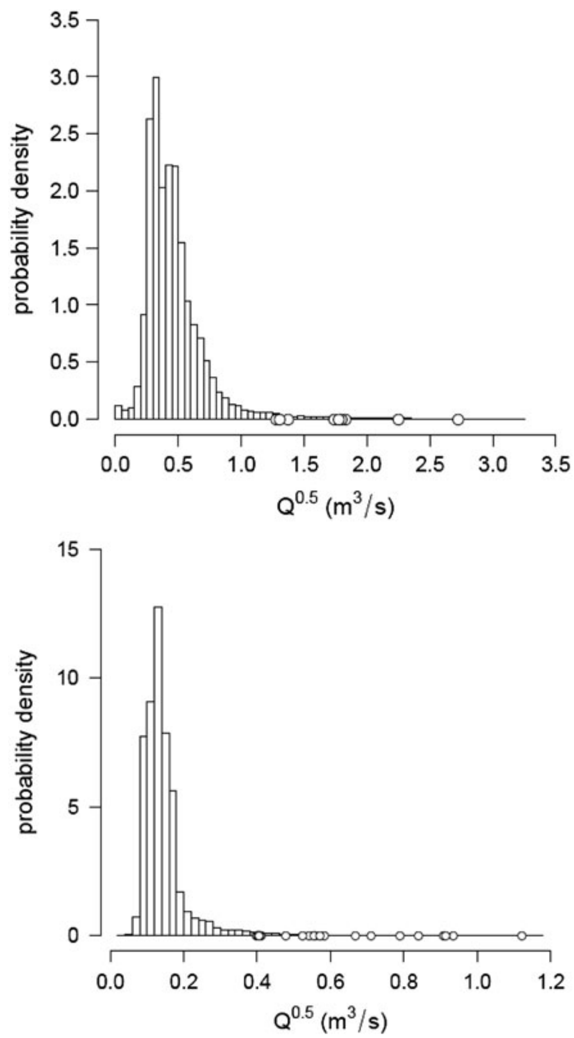

Fig. 2 Discharge distribution in the catchments of Leupegem (*top*) and Muizen (*down*) during the period 2006–2008. All other sampled catchments had similarly skewed distributions. The maximal discharge observed during the sampled peak events is indicated as *open white dots* on the high discharge end of the distribution

(shown in Fig. 3 for the catchments of Leupegem and Muizen, representative for the other catchments). Most relationships were highly significant (Table 2). The ratio of ASi/DSi in the samples followed a similar relation as ASi concentrations (Fig. 3; Table 2).

Suspended matter and TOC concentrations

Except for the catchment of Etikhove, SPM concentration showed a highly significant positive linear correlation with ASi concentration (Table 3). Four catchments showed a significant negative correlation between the relative ASi-content in the riverine SPM and the SPM concentration (Table 3; Fig. 4). The observed decrease in relative amount of ASi in SPM was highest at low SPM concentrations and smoothed at highest measured SPM concentrations: at high SPM concentrations, the ratio ASi/SPM was around 0.2% for all sampled streams. Where analyzed, the relative amount of ASi increased significantly with the relative amount of organic matter (TOC) in transported SPM (Fig. 5).

Annual load

During peak flow events, the decreasing DSi concentration was largely compensated by (1) increases in discharge and (2) increases in ASi concentration. Consequently, DSi and ASi transport and the resulting net transported total bio-reactive Si (TSi = ASi + DSi) increased significantly during peak flow periods. The contribution of ASi to TSi transport rose from near 0% during base flow periods to values up to 80% during peak flow events.

On a yearly basis we estimate that 6–40% of all bio-reactive Si was transported as ASi (Table 4). While around 35–45% of all water was transported during peak flow events, 68–75% of all ASi and 25–36% of all DSi was transported at the same time (Table 4). The fluctuations of ASi and DSi fluxes, discharge and contribution of ASi flux to total bio-reactive Si flux is shown in detail for the year 2007 for the catchment of Leupegem in Fig. 6.

Discussion

We showed that significant amounts of ASi are mobilized during precipitation events in catchments dominated by cropland in the Loam Belt in Flanders. At highest discharges, ASi even became the dominant type of transported bio-reactive Si (ASi + DSi). The estimates had a large uncertainty resulting from the large variability of observed DSi but especially ASi concentrations around the fitted Si–*Q* relationships. Also, as ASi is strongly associated with peak flow events during which soil erosion occurs, our estimate will vary in function of the events sampled during the observation period. At the lower confidence limit,

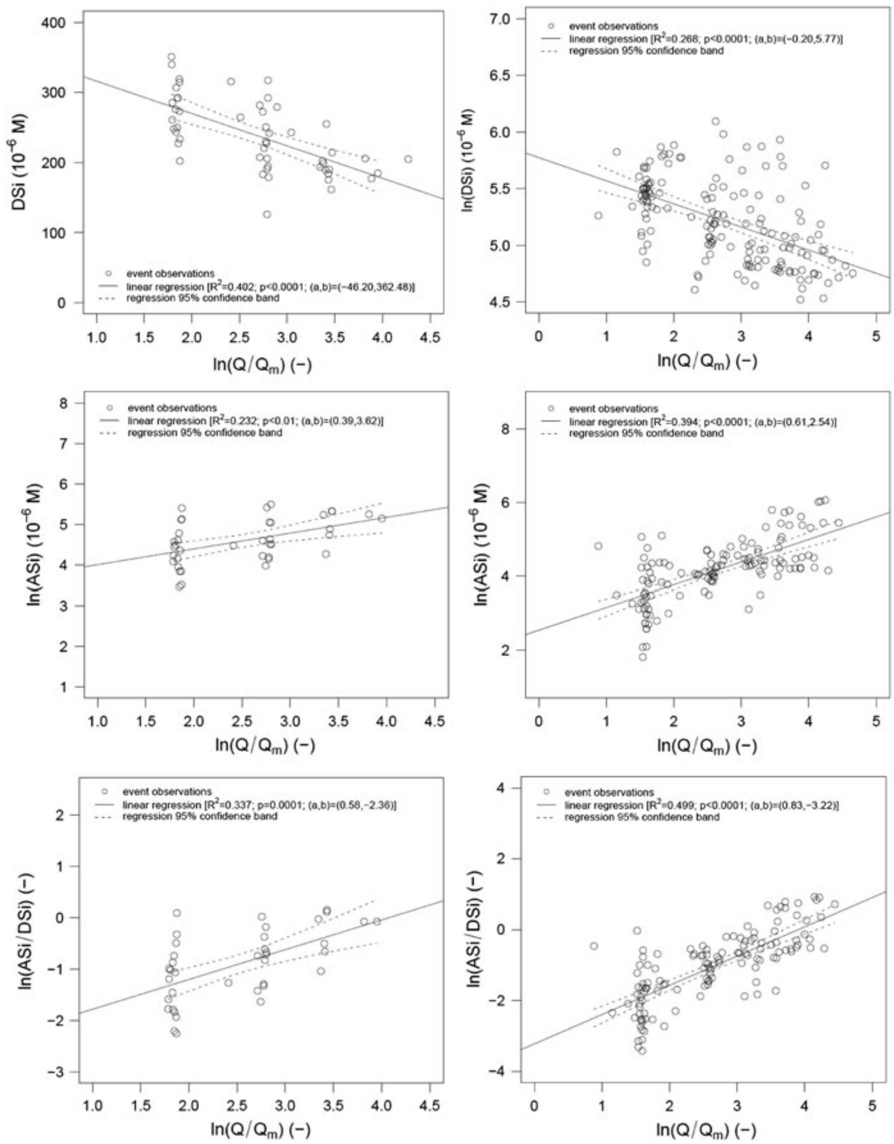

Fig. 3 Relations between relative discharge (Q/Q_{modal}) and DSi and ASi concentrations and relative importance of ASi (ASi/DSi) in the catchments of Leupegem (*left*) and Muizen (*right*). Q_{modal} is modal discharge from 2006 to 2008

6–8.5% of all bio-reactive Si was transported as ASi, while this was 20–40% at the higher limit.

Ecosystem amorphous Si pools are largest in the upper soil layers (e.g. Blecker et al. 2006): erosion induces a significant mobilization of topsoil and hence ASi from terrestrial ecosystems, resulting in the strong correlation between ASi and SPM concentrations we observed. ASi concentrations were related to TOC concentrations, indicating that ASi in the soils and sediment is preferably associated with organic matter. Considering the fact that phytoliths are a major source of ASi, the latter is not surprising (Conley 2002). This association may also explain why ASi/SPM ratios decrease with increasing SPM concentrations. Previous research has shown that exported sediments are enriched in organic matter and clay during relatively short-term small events, while this is not the case later during large events characterized by higher peak discharges (Steegen et al. 2000, 2001). ASi is mainly associated with organic matter, and the ASi/SPM ratio is expected to decrease with increasing event intensity (towards higher peak discharges), higher SPM concentration and lower relative organic matter content. The association between ASi and phytoliths could also explain why catchments with substantial grassland

Table 2 Significance, R^2 and slope of linear relationships between relative discharge (Q/Q_m) and dissolved Si (DSi), amorphous Si (ASi) and ASi/DSi (ratio of ASi and DSi concentration), respectively, in all sampled catchments during the studied peak events

Catchment	Respons variable	Predictor variable	R^2	p value	Slope
Maarke Kerkem	DSi	Q/Q_m	0.243	<0.01	−1.84
	ln(ASi)	Q/Q_m	0.129	NS	0.0239
	ln(ASi/DSi)	Q/Q_m	0.171	NS	0.0313
Leupegem	DSi	$\ln(Q/Q_m)$	0.402	<0.0001	−46.2
	ln(ASi)	$\ln(Q/Q_m)$	0.232	<0.01	0.390
	ln(ASi/DSi)	$\ln(Q/Q_m)$	0.337	<0.001	0.579
Broekbeek	DSi	$\ln(Q/Q_m)$	0.512	<0.0001	−68.3
	ASi	Q/Q_m	0.926	<0.0001	19.1
	ASi/DSi	Q/Q_m	0.898	<0.0001	0.0762
Etikhove	DSi	$\ln(Q/Q_m)$	0.122	NS	−17.6
	ASi	$\ln(Q/Q_m)$	0.924	<0.0001	129
	ln(ASi/DSi)	$\ln(Q/Q_m)$	0.947	<0.0001	0.53
Velm	ln(DSi)	$\ln(Q/Q_m)$	0.182	<0.001	−0.274
	ASi	$\ln(Q/Q_m)$	0.702	<0.0001	80.7
	ASi/DSi	$\ln(Q/Q_m)$	0.774	<0.0001	0.356
Muizen	ln(DSi)	$\ln(Q/Q_m)$	0.268	<0.0001	−0.204
	ln(ASi)	$\ln(Q/Q_m)$	0.394	<0.0001	0.612
	ln(ASi/DSi)	$\ln(Q/Q_m)$	0.499	<0.0001	0.826
Wellen	ln(DSi)	Q/Q_m	0.344	<0.001	−0.0441
	ln(ASi)	$\ln(Q/Q_m)$	0.312	<0.01	0.580
	ln(ASi/DSi)	$\ln(Q/Q_m)$	0.391	<0.001	0.864
Piringen	ln(DSi)	$\ln(Q/Q_m)$	0.091	NS	−0.134
	ln(ASi)	$\ln(Q/Q_m)$	0.422	<0.001	0.906
	ln(ASi/DSi)	$\ln(Q/Q_m)$	0.347	<0.001	1.03

It is indicated whether data were log-transformed to normalize (in case of normality, no log-transformation was applied)

NS not significant, Q discharge, Q_m modal discharge 2006–2008

Table 3 The significance, R^2 and slope of linear relationships between suspended matter concentrations (SPM) and ASi concentrations [ASi] and relative ASi content of the sediment (ASi/SPM), respectively, in all sampled catchments during peak events

Location	Respons variable	Predictor variable	p value	R^2	Slope
Maarke Kerkem	ln[ASi]	SPM	<0.01	0.457	0.38
Leupegem	ln[ASi]	SPM	<0.0001	0.610	0.27
Broekbeek	[ASi]	SPM	<0.0001	0.941	51.7
Etikhove	[ASi]	SPM	NS		
Velm	[ASi]	SPM	<0.0001	0.746	74.0
Muizen	ln[ASi]	SPM	<0.0001	0.515	0.3
Wellen	ln[ASi]	SPM	<0.05	0.198	0.98
Piringen	ln[ASi]	SPM	<0.0001	0.552	0.34
Maarke Kerkem	ASi/SPM	SPM	NS		
Leupegem	ASi/SPM	ln(SPM)	<0.0001	0.500	−0.086
Broekbeek	ASi/SPM	ln(SPM)	NS	0.329	−0.055
Etikhove	ln(ASi/SPM)	ln(SPM)	<0.01	0.609	−0.687
Velm	ASi/SPM	ln(SPM)	<0.0001	0.697	−0.312
Muizen	ASi/SPM	SPM	NS		
Wellen	ASi/SPM	SPM	NS		
Piringen	ln(ASi/SPM)	SPM	<0.05	0.173	−0.095

It is indicated whether data were log-transformed or not

NS not significant

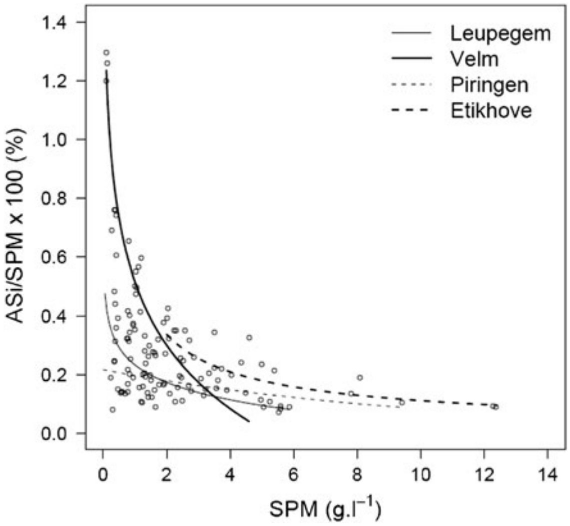

Fig. 4 Decrease in relative amount of amorphous Si (ASi) in suspended matter (SPM) with increasing SPM concentrations, in the four catchments where a significant exponential decrease was observed

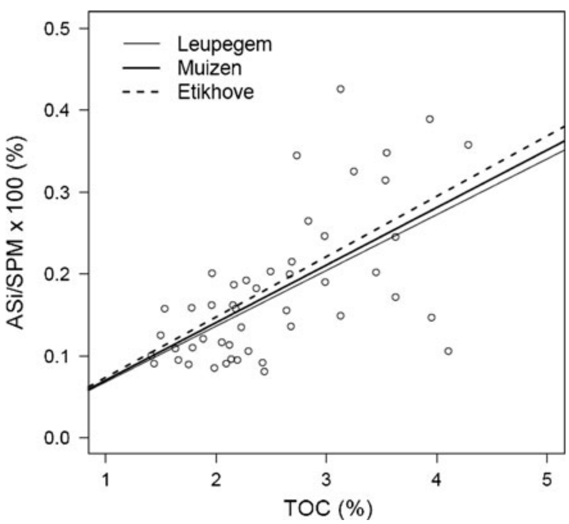

Fig. 5 Relation between total organic carbon (TOC) and amorphous Si (ASi) content in suspended matter (SPM) in the catchments of Leupegem, Muizen and Etikhove. The *lines* represent the position of the different catchments within the data. All linear regressions were highly significant ($p < 0.0001$; $R^2 > 0.81$)

cover were generally associated with higher transported ASi/TSi ratios. Grasses are significant accumulators of ASi (Hodson et al. 2005): grassland soils have a large soil phytolith pool (Blecker et al. 2006).

A trade-off between DSi and ASi

We observed a tight connection between the speciation of silica mobilized from cropland dominated catchments and discharge. During base flow, almost all silica was found in the form of DSi. The minor importance of diatom growth in the sampled catchments was confirmed by negligible ASi-concentrations during base flow in this study, and year-round measurements at base flow in 51 Flemish river basins (Struyf et al., unpublished data). During peak events, a clear trade-off existed between DSi and ASi concentrations, and ASi often became the dominant form of transported bio-reactive Si. The sharp initial decrease in DSi concentration during peak events originates in the transition from direct input of DSi rich groundwater and deep soil water towards diluted surface soil water and overland flow at the start of a runoff event. SPM and ASi concentrations in suspension both increase during the rising limb of the peak event. Yet, as explained above, the ASi content (% of transported material) of the mobilized sediment decreased exponentially when discharge increased. Still, as SPM concentrations generally increase with increasing discharge (Steegen et al. 2000), the ASi concentration (per unit of water) increases with increasing discharge.

The dynamics of the continental ASi pool

As in most of Western Europe, land use in Flanders has shifted from almost completely forest-dominated to merely 11% of forest cover over the past two millennia (Hermy et al. 2008): only 16% of these forests are older than 250 years. Although often more severe in Flanders than many other regions, deforestation and forest fragmentation is a global problem (Riitters et al. 2000). In general, human land use changes will result in an enhanced sensitivity of land surface to erosion, although this can strongly depend on management practices and structure of the particular watershed (Walling 1999). Our results clearly show that land use changes, impacting on erosion, should be related to changing silica dynamics. Our plots are representative for cropland dominated watersheds as widely found in Western Europe, where deforestation and subsequent cultivation of land results in the enhanced erosion of topsoil (Rommens et al. 2006). The Scheldt estuary itself is

Table 4 Percentage of the total load of bio-reactive Si (TSi) transported as ASi in all catchments, based on yearly load calculations for 2007

Station	*r*	ASi/TSi (%)			DSi: PF/TF (%)			ASi: PF/TF (%)		
		l confidence	Mean	u confidence	l confidence	Mean	u confidence	l confidence	Mean	u confidence
Leupegem	0.70	0.08	0.17	0.35	0.28	0.30	0.31	0.65	0.67	0.63
	0.75	0.08	0.17	0.34	0.34	0.36	0.37	0.72	0.74	0.70
	0.80	0.09	0.18	0.33	0.41	0.43	0.45	0.78	0.80	0.77
Maarke Kerkem	0.60	0.07	0.15	0.42	0.25	0.24	0.24	0.88	0.70	0.38
	0.70	0.08	0.16	0.39	0.31	0.30	0.29	0.91	0.77	0.48
	0.80	0.10	0.17	0.35	0.43	0.43	0.42	0.95	0.86	0.66
Broekbeek	0.70	0.08	0.08	0.08	0.08	0.09	0.09	0.40	0.40	0.40
	0.80	0.08	0.08	0.09	0.11	0.12	0.13	0.45	0.45	0.45
	0.90	0.09	0.09	0.09	0.24	0.25	0.26	0.59	0.59	0.59
Etikhove	0.60	0.40	0.41	0.43	0.27	0.29	0.30	0.72	0.59	0.45
	0.70	0.40	0.40	0.42	0.32	0.34	0.35	0.78	0.67	0.52
	0.80	0.41	0.40	0.41	0.41	0.44	0.44	0.86	0.77	0.64
Velm	0.70	0.03	0.04	0.05	0.04	0.05	0.06	0.62	0.53	0.42
	0.80	0.04	0.04	0.05	0.07	0.08	0.09	0.72	0.65	0.57
	0.90	0.04	0.04	0.05	0.18	0.20	0.23	0.82	0.78	0.72
Muizen	0.70	0.06	0.11	0.27	0.21	0.21	0.22	0.83	0.68	0.42
	0.75	0.06	0.11	0.24	0.25	0.25	0.26	0.88	0.75	0.50
	0.80	0.06	0.11	0.22	0.30	0.30	0.31	0.91	0.80	0.59
Wellen	0.70	0.03	0.05	0.10	0.08	0.09	0.09	0.40	0.40	0.40
	0.80	0.03	0.05	0.10	0.11	0.12	0.13	0.45	0.45	0.45
	0.90	0.03	0.06	0.11	0.24	0.25	0.26	0.59	0.59	0.59

The percentage of DSi and ASi transported during peak events is indicated (PF/TF, peak flow/total flow)

The calculation was repeated for three different *r*-values. The *r*-value is the ratio of base flow discharge, modelled by using WETSPRO (Willems 2009), to measured discharge, used as criterion to differentiate between peak and base flow. The upper (u) respectively lower (l) (67% confidence) and mean confidence interval for ASi contribution to yearly fluxes was based on respectively upper, lower and mean values for a and b in the fitted ASi–Q relationships (ASi $= aQ + b$) and respectively lower, upper and mean values for a en b in the fitted DSi–Q relationships (DSi $= aQ + b$)

characterized by large fluxes of SPM (Soetaert et al. 2006). These fluxes mostly result from the large-scale mobilization of sediments in the cultivated catchments (Verlaan 2000; Verstraeten et al. 2003). In such watersheds, it is clear that ASi dynamics should be included in silica transport budgets. Erosion physically mobilizes the ASi layers from the soil surface of the terrestrial ecosystems, and mobilizes them as suspended ASi into riverine systems. Recent research has emphasized the importance of these ASi rich surface soils as buffers in terrestrial Si biogeochemistry, effectively controlling mineral weathering fluxes through biological uptake (Conley 2002; Derry et al. 2005; Street-Perrott and Barker 2008; Conley et al. 2008; Struyf and Conley 2009). The physical removal of this important ASi rich surface soil layers in agricultural watersheds, will also impact the controlling effect these layers have on Si transport through watersheds.

The fate of the mobilized ASi is uncertain: previous research suggests that significant amounts are deposited in wetlands (Struyf et al. 2009) or lakes (Humborg et al. 1997). The magnitude of (re-)deposition will depend on the characteristics of the stream network as well as its management. Earlier works showed that the ASi deposition rate in tidal marshes along the Scheldt estuary was strongly correlated with the sediment deposition rate (Struyf et al. 2007a). Depending on the management, and the structure of the watershed (lakes, large floodplains,…), ASi will be redistributed over the landscape, or will end up as transported towards the coastal zone.

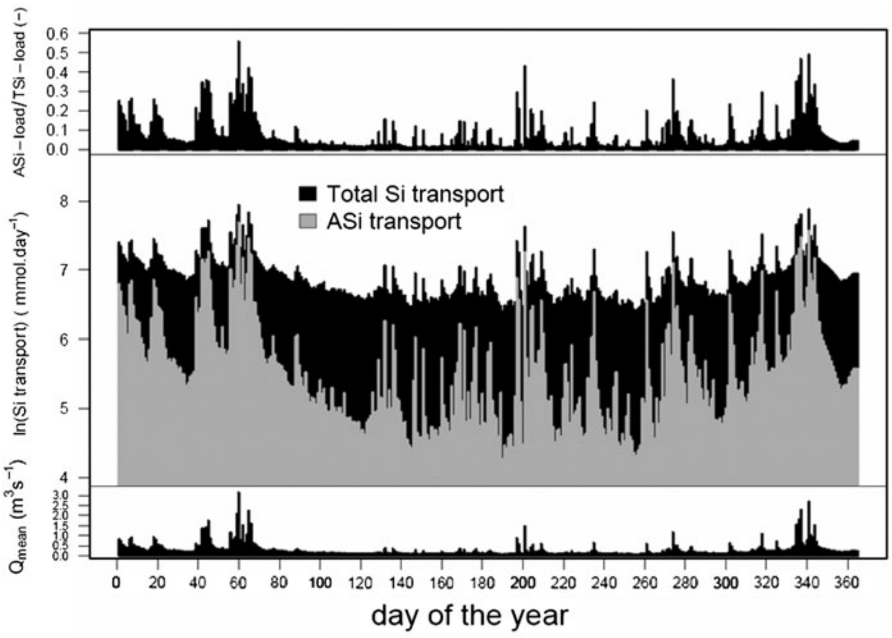

Fig. 6 Time series of discharge, simulated ASi and TSi (ASi + DSi) fluxes and ASi/TSi ratios for the catchment of Leupegem during 2007. Simulated silica loads were calculated following the peak flow scenario "$r = 0.75$"* and are shown as daily summed values. Q_{mean} represents the daily averaged discharge. Attention must be paid to the logarithmic (log) scale of each middle graph. * See Table 4

Our results further emphasize the importance of precipitation events in the terrestrial Si dynamics. Following global change models, hydrological characteristics at the continental scale in Europe are expected to change. The flood disaster frequency is projected to increase in Europe, especially in eastern and northern Europe and the Atlantic coast and central Europe (IPCC 2008). Higher flows are expected during peak flow periods, while lower flows are expected during base flow periods (Arnell 2003, 2004). Moreover, the intensity of daily precipitation events is expected to increase (e.g. Christensen and Christensen 2003; Kjellström 2004; Kundzewicz et al. 2005). Associated, the suspended sediment yield is also expected to increase: in the Meuse basin (close to the Scheldt basin), SPM transport is estimated to increase with 8–12% in the twenty-first century compared to the twentieth century (Ward et al. 2009). Based on our observations, such hydrological changes will coincide with drastic changes in ASi and DSi dynamics in the river continuum. While DSi is mainly associated with base flow, ASi was almost completely transported during peak events. Increased intensity and occurrence frequency of events will result in increasing importance of ASi transport in total reactive Si transport at the scale of low-order watersheds, especially during the winter season, when rain intensity is expected to increase (Middelkoop et al. 2001). Reduced precipitation in summer, and higher drought frequency (Middelkoop et al. 2001), as expected in Western Europe, could lower fluxes of DSi from low-order river basins during the summer season. This is exactly the period when downstream in estuaries and coastal zones DSi is potentially limiting production of diatoms (Cloern 2001). The combination of land use changes and associated erosion sensitivity, changing hydrographs due to climate change and poorly constrained ASi dynamics in upstream ecosystems, currently results in a poor quantification of ASi and DSi mobilization at the lowest river-order scale. In recent work (Thieu et al. 2009), DSi concentration in surface run-off and base flow is still considered identical, and ASi dynamics in relation to discharge are not accounted for. The incomplete understanding of hydrology related dynamics of Si mobilization, and incomplete understanding of the biological storage and processing of Si as ASi, explain the major differences (up to 200% and more) between modelled and observed Si fluxes at the catchment scale, even in these most recent modelling efforts (e.g. Thieu et al. 2009).

Conclusions

Our work is the first to show the importance of ASi transport in silica budgets in cultivated catchments.

We observed that up to 40% of yearly transported bio-reactive Si in these cultivated catchments is transported as ASi. Yet, the dynamics of bio-reactive Si cycling in erosion-sensitive catchments are currently poorly constrained. Several questions need focus before we can quantify the importance of this cultivation impact on local Si dynamics for continental Si transport:

– Where is ASi deposited in the river continuum, and what are the timescales at which it is stored or recycled?
– At what timescales is ecosystem ASi mobilized after transformation of e.g. a forest into a cropland? Does the intensity of ASi dissolution and erosion change in time?
– How do erosion management techniques like riparian buffer zones and sediment capture ponds impact on re-allocation of terrestrial ASi over neighbouring ecosystems?
– What is the effect of sediment management in rivers (e.g. dredging) on bio-available silica if more Si would be transported to rivers as ASi?

Our results emphasize tackling these research questions are important. Future research is suggested to focus on (1) the "on-field" path of ASi in relation to mineral sediments and (2) the "in-stream" path followed by terrestrial ASi towards the river mouth after mobilization in the upper parts of the basin. Also the different dynamics of DSi and ASi under high discharge conditions need to be accounted for in watershed scale Si balances.

Acknowledgments Eric Struyf would like to thank FWO (Research Foundation Flanders) for personal post doc research funding. We would like to acknowledge Belgian Science Policy (BELSPO: SD/NS/05a) for funding project "LUSi: Land use changes and silica fluxes in the Scheldt river basin" and FWO for funding project "Tracking the biological control on Si mobilization in upland ecosystems" (Project nr. G014609N). Wim Clymans thanks IWT for personal research funding. We would like to thank Tom Van der Spiet and Anne Cools for all analyses.

References

Arnell NW (2003) Relative effects of multi-decadal climatic variability and changes in the mean and variability of climate due to global warming: future streamflows in Britain. J Hydrol 270:195–213

Arnell NW (2004) Climate change and global water resources: SRES emissions and socio economic scenarios. Glob Environ Change 14:31–52

Blecker SW, McCulley RL, Chadwick OA et al (2006) Biologic cycling of silica across a grassland bioclimosequence. Glob Biogeochem Cycles 20:GB3023

Christensen JH, Christensen OB (2003) Severe summertime flooding in Europe. Nature 421:805–806

Clarke J (2003) The occurence and significance of biogenic opal in the regolith. Earth Sci Rev 60:175–194

Cloern JE (2001) Our evolving conceptual model of the coastal eutrophication problem. Mar Ecol Prog Ser 210:223–253

Conley DJ (1997) Riverine contribution of biogenic silica tot the oceanic silica budget. Limnol Oceanogr 42: 774–777

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Glob Biogeochem Cycles 16: GB1121

Conley DJ, Schelske CL (2001) Biogenic silica. In: Smol JP, Birks HJB, Last WM (eds) Tracking environmental change using lake sediments: biological methods and indicators. Kluwer Academic Press, Dordrecht, pp 281–293

Conley DJ, Schelske CL, Stoermer EF (1993) Modification of the biogeochemical cycle of silica with eutrophication. Mar Ecol Prog Ser 101:179–192

Conley DJ, Likens GE, Buso DC et al (2008) Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. Glob Change Biol 14: 2548–2554

Derry LA, Kurtz AC, Ziegler K et al (2005) Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature 433:728–731

Dugdale RC, Wilkerson FP, Minas HJ (1995) The role of a silicate pump in driving new production. Deep Sea Res I 42:697–719

Dürr HH, Meybeck M, Hartmann J (2009) Global spatial distribution of natural riverine silica inputs to the coastal zone. Biogeosciences 6:1345–1401 (Discussions)

Fabres J, Tesi T, Velez J et al (2008) Seasonal and event-controlled export of organic matter from the shelf towards the Gulf of Lions continental slope. Cont Shelf Res 28:1971–1983

Gérard F, Mayer KU, Hodson MJ et al (2008) Modelling the biogeochemical cycle of silicon in soils: application to a temperate forest ecosystem. Geochim Cosmochim Acta 72:741–758

Gouze E, Raimbault P, Garcia N et al (2008) Nutrient and suspended matter discharge by tributaries into the Berre Lagoon (France): the contribution of flood events to the matter budget. C R Geosci 340:233–244

Hermy M, Van Der Veken S, Van Calster H et al (2008) Forest ecosystem assessment, changes in biodiversity and climate change in a densely populated region (Flanders, Belgium). Plant Biosyst 142:623–629

Hodson MJ, White PJ, Mead A, Broadley MR (2005) Phylogenetic variation in the silicon composition of plants. Ann Bot 96:1027–1046

Humborg C, Ittekkot V, Cociasu A et al (1997) Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386:385–388

Kjellström E (2004) Recent and future signatures of climate change in Europe. Ambio 23:193–198

Kundzewicz ZW, Ulbrich U, Brücher T et al (2005) Summer floods in Central Europe climate change track? Nat Hazards 36:165–189

Middelkoop H, Daamen K, Gellens D, Grabs W, Kwadijk JCJ, Lang H, Parmet B, Schadler B, Schulla J, Wilke K (2001) Impact of climate change on hydrological regimes and water resources management in the rhine basin. Clim Change 49:105–128

Rabosky DL, Sorhannus U (2009) Diversity dynamics of marine planktonic diatoms across the Cenozoic. Nature 457:183–186

Ragueneau O, Tréguer P, Leynaert A et al (2000) A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. Glob Planet Change 26:317–365

Riitters K, Wickham J, O'Neill R et al (2000) Global-scale patterns of forest fragmentation. Conserv Ecol 4(3)

Rommens T, Verstraeten G, Bogman P et al (2006) Holocene alluvial sediment storage in a small river catchment in the loess area of central Belgium. Geomorphology 77: 187–201

Soetaert K, Middelburg JJ, Heip C et al (2006) Long-term change in dissolved inorganic nutrients in the heterotrophic Scheldt estuary (Belgium, The Netherlands). Limnol Oceanogr 51:409–423

Steegen A, Govers G, Nachtergaele J et al (2000) Sediment export by water from an agricultural catchment in the Loam Belt of central Belgium. Geomorphology 33:25–36

Steegen A, Govers G, Takken I et al (2001) Factors controlling sediment and phosphorus export from two Belgian agricultural catchments. J Environ Qual 30:1249–1258

Street-Perrott AF, Barker PA (2008) Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon. Earth Surf Proc Land 33:1436–1457

Struyf E, Conley DJ (2009) Silica: an essential nutrient in wetland biogeochemistry. Front Ecol Environ 7:88–94

Struyf E, Temmerman S, Meire P (2007a) Dynamics of biogenic Si in freshwater tidal marshes: Si regeneration and retention in marsh sediments (Scheldt estuary). Biogeochemistry 82:41–53

Struyf E, Van Damme S, Gribsholt B et al (2007b) *Phragmites australis* and silica cycling in tidal wetlands. Aquat Bot 87:134–140

Struyf E, Opdekamp W, Backx H et al (2009) Vegetation and proximity to the river control amorphous Si storage in a riparian wetland (Bierbza National Park, Poland). Biogeosciences 6:623–631

Thieu V, Billen G, Garnier J (2009) Nutrient transfers in three contrasting NW European watersheds: the Seine, Somme, and Scheldt rivers. A comparative application of the Seneque/Riverstrahler model. Water Res 43(6):1740

Tréguer P, Pondaven P (2000) Global change—silica control of carbon dioxide. Nature 406:358–359

Tréguer P, Nelson DM, Vanbennekom AJ et al (1995) The silica balance in the world ocean—a reestimate. Science 268:375–379

Trenberth KE, Dai AG, Rasmussen RM et al (2003) The changing character of precipitation. Bull Am Meteorol Soc 84:1205

Van Cappellen P (2003) Biomineralization and global biogeochemical cycles. Rev Miner Geochem 54:357–381

Verlaan PAJ (2000) Marie vs fluvial bottom mud in the Scheldt Estuary. Estuar Coast Shelf Sci 50:627–638

Verstraeten G, Van Rompaey A, Poesen J et al (2003) Evaluating the impact of watershed management scenarios on changes in sediment delivery to rivers? Hydrobiologia 494:153–158

Vorosmarty CJ, Fekete BM, Meybeck M et al (2000) Global system of rivers: its role in organizing continental land mass and defining land-to-ocean linkages. Glob Biogeochem Cycles 14(2):599–621

Walkley A, Black IA (1934) An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci 37:29–38

Walling DE (1999) Linking land use, erosion and sediment yields in river basins. Hydrobiologia 410:223–240

Ward PJ, van Balen RT, Verstraeten G et al (2009) The impact of land use and climate change on late Holocene and future suspended sediment yield of the Meuse catchment. Geomorphology 103:389–400

Willems P (2009) A time series tool to support the multicriteria performance evaluation of rainfall-runoff models. Environ Model Softw 24:311–321

Woodward J, Foster I (1997) Erosion and suspended sediment transfer in river catchments: environment controls, processes and problems. Geography 82:353–376