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LAND USE AND SILICA FLUXES THROUGH THE SCHELDT RIVER BASIN

"LUSI"

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North Sea

FINAL REPORT PHASE 1

LAND USE AND SILICA FLUXES THROUGH THE SCHELDT RIVER BASIN

"LUSI"

SD/NS/05A

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July 2010

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P. Meire, G. Govers, B. Van Wesemael . ***Land use and silica fluxes through the Scheldt river basin "LUSI"*** Final Report Phase 1. Brussels : Belgian Science Policy 2010 – 45p. (Research Programme Science for a Sustainable Development :

1. Background and objectives

Eutrophication

Eutrophication of rivers, estuaries and coastal waters has received increasing attention since the 1980's, when water quality in many water bodies suffered from increasing anthropogenic pressure, such as urbanization, industrialization and agricultural activities (e.g. Schelske et al. 1983, Lancelot 1995). The problem is not purely of an "ecological nature": the goods and services provided by estuarine systems are such, that they have been highlighted as the economically most valuable ecosystems in the world (Costanza et al. 1997). Essentially, eutrophication is triggered by excess input of the nutrients N and P into the aquatic ecosystems. In coastal waters, and also in estuaries, the nutrient ratios can as a result be altered so drastically that the food web can degenerate by shifts in phytoplankton communities. Generally, diatoms have a competitive advantage over other algae, because of a higher photosynthetic capacity and lower maintenance energy requirements (Billen et al. 1991). Diatoms have therefore been identified as the main energetic source for the estuarine and coastal food chain (Sullivan & Moncreiff 1990). In contrast to other algae taxa, diatoms require about equal amounts of N and Si (optimal growth at N-P-Si ratios of 16-16-1) (Redfield 1958, Justic et al. 1995). An over delivery of N and P can lead to Si-limitation of diatoms. When diatoms become Si-limited, this can induce a succession of a diatom-dominated phytoplankton community towards a community dominated by non-diatom species, with catastrophic results for the coastal food web. The North Sea is, because of the high human pressure in adjacent river basins and its enclosed nature, highly vulnerable for eutrophication (Ducrotoy et al. 2000): understanding precisely the mechanisms contributing to eutrophication in the North Sea is a necessity for effective remediation.

The unknown Si component

Nutrient concentrations in the North Sea and adjacent estuaries are the end-result of basin-wide input, retention, mobilization and transport of N, P and Si. Traditionally, eutrophication has been approached as a problem of increased human inputs of N and P. In contrast, dissolved Si concentrations have mostly been considered as not anthropogenically influenced. Transfer of dissolved Si (DSi) to rivers has usually been considered to result from a pure geochemical process, involving only direct chemical weathering of soil minerals. As such, the DSi emission from terrestrial systems affected by human activities into water bodies has been considered relatively constant compared to pristine natural systems. Uptake by diatoms in the river continuum was the main factor used to explain DSi profile changes through time.

Current research has clearly pointed out that vegetation cover can have a strong impact on the fluxes of Si through terrestrial ecosystems. It has become clear that ecosystems can store a large amount of Si as amorphous, biogenic Si (amorphous SiO_2nH_2O, ASi), both in soil and vegetation (Conley 2002). ASi is far more soluble than mineral Si, and terrestrial Si fluxes are thus potentially strongly controlled by biota. As a result, land use changes and concurrent changes in vegetation cover, have a strong potential impact on the fluxes of Si through river basins.

Still, the release of DSi from different terrestrial systems in river basins has never before been quantified with respect to land use changes. Current knowledge is insufficient to quantify how land use change might have influenced the transport of Si through river basins towards the coastal zone. Such information is however essential for our understanding of eutrophication problems from the upstream aquatic ecosystems way down to the North Sea (Cloern 2001). As the release of DSi counteracts eutrophication effects, quantifying the role of land use on its emission can lead to a revision of water quality objectives and maintenance objectives. In fact, the history of DSi-emission may have influenced the carrying capacity for primary production much more than is shown by current ecological models. Here lies the relevance of this study.

Objectives

This project aims to answer the question if Si fluxes through a river basin, and ultimately towards the sea, can change because of land use changes. These changes will be budgeted for the Scheldt basin, taking into account surface runoff, subsurface drainage and storage and cycling through vegetation. The results will be used to evaluate the effect of land use changes over historical times on Si fluxes. Moreover, it is the aim to formulate recommendations towards land planning with respect to the reduction of eutrophication, working from the viewpoint of Si in the nutrient ratios. As such, this study of Si can provide a mirror image for the N and P side of the eutrophication problem, and provide invaluable, new insights in our evolving concept of eutrophication (Cloern 2001).

Habitat scale research towards surface erosion and subsurface transport of dissolved Si and amorphous Si and sediments (as an indicator for transport of mineral Si) will be conducted in different landscape types. On a Scheldt basin scale scale, rivers draining sub-basins, will be sampled on a regular basis for all BSi and DSi. The sampled sub-basins will represent a gradient from still largely forested to largely covered by cropland. The integration of results from both site-specific experiments and basin scale sampling will for the first time allow an estimate, based on both historical and recent land use maps, of the extent to which Si fluxes towards the coastal zone have been altered by human land use, and how this change has been triggered by changes in erosion processes, changes in vegetation type and cover, and hydrology.

Expected outcomes

- to quantify site-specific differences in surface transport of Si during rain events and in subsurface transport of Si in soil-water, in different (differing in slope, soil and hydrology characteristics) forest ecotypes and agricultural sites characterising the variability occurring in the Scheldt basin

- to establish a basin-scale relation between land use and Si transport through rivers, by quantifying the discharge and concentration of suspended matter, ASi and DSi in at least 40 sub-basins with different ratios in land use types (agriculture, forest,…).

- to provide the evaluation of changes in basin-wide Si transport to an estuary and eventually the coastal zone, as a result of land use changes, by applying the results obtained in the Scheldt watershed from the experiments and sampling campaigns, to maps of historical land use

2. Methodology

Experiments and sampling within this project are conducted at different temporal and spatial scales:

- Habitat and small catchment scale research is aimed at unraveling the processes which underlie the observed fluxes of different Si components in the end-members receiving the Si components: rivers. Detailed research towards Si mobilization at habitat scales is implemented to unravel how local erosion conditions, vegetation and hydrological characteristics influence the transport of both particulate and dissolved Si in different types of land use.
- A sub-basin scale sampling campaign maps the Si fluxes through the river continuum of the Scheldt basin towards the North Sea, and the influence of land use on the basin-scale transport of Si.

Land use and habitat scale Si mobilization

Understanding human impact on Si transport requires an assessment of the relative importance of various pathways of Si mobilization for different land use types. At the local scale (parcel or hill slope), we need to determine how Si is transported through surface and subsurface pathways under various land use types. Field sites for habitat scale research were selected early during the project. The selected sites represent one soil texture type, common in the Scheldt basin (loam).

Assessment of surface runoff on the scale of a single agricultural parcel or a small sub-catchment

In each of the selected catchments, during rain events, runoff of suspended material, ASi and DSi were experimentally quantified from agricultural parcels and small agricultural sub-catchments.

Rainfall simulation experiments were carried out on the small plot scale (1 m^2) using a well-established protocol on arable land with varying crops and with varying tillage techniques (winter and summer crops and conventional vs. non-inversion tillage). The experiments were carried out with a fixed rainfall intensity of ca. 45 mm/h. Before and after the experiments a series of measurements was taken to characterise the experimental conditions: soil moisture content, soil bulk density, texture and organic matter content. During the experiments runoff generation is monitored and samples are taken at regular time intervals and processed in the laboratory in order to determine sediment, Si content and sediment quality (grain size, organic C content…).

Although rainfall simulation experiments allow to identify the fundamental controls on runoff generation and on sediment production (and presumably also on Si fluxes), the quantitative results cannot be linearly extrapolated to larger areas as scale effects are important. Re-infiltration of runoff and re-deposition of sediment may occur and the relative importance of inter-rill, rill and gully erosion may change so that the quality of the deposited and exported sediment may differ fundamentally from that of the eroded sediment. Therefore monitoring at the small catchment scale is also important. This part of the research was performed at monitoring stations operated by UCL and K.U.Leuven K.U.Leuven operates a set of 6 experimental plots of 180 m² in Huldenberg, central Belgium, where runoff and erosion are continuously measured by collecting a fixed ratio of the runoff and the bulk of the sediment in containers. The runoff collector of these plots are equipped with automatic water level recorders. On the site a weather station is installed. Data are directly transmitted to the internet. UCL operates a 200 ha catchment near Sint-Truiden in central Belgium where runoff and sediment export are continuously monitored using a water level logger and a flow-proportional pumping sampler. By analysing samples from these monitoring sites for sediment quantity, sediment quality and Si content, it was possible to understand how Si fluxes change with increasing catchment area and how these changes relate to changes in sediment quality and runoff. Furthermore, these data provide insight in the role of event magnitude and potential seasonality in Si transport.

Subsurface (quick flow and base flow) mobilization of Si in different land use types

Land-use cannot only change surface runoff of particulate and biogenic Si. Vegetation can take up large amounts of Si and store it in siliceous bodies known as phytoliths. Dissolved Si is only released from the phytoliths during the plants decay (Raven 2003). The amount of DSi taken up by plants and stored as ASi differs among plant species. Grasses (crops) are known to strongly accumulate Si (Conley 2002). The harvest of crops might remove large amounts of

ASi from the system. Dense plant covers can increase the chemical weathering (through acidic exudations, association of roots with micro-organisms) and porosity of soils, thus encouraging percolation and concurrent enrichment with DSi of rainwater. Buried phytoliths, available for dissolution, could enrich percolating water with DSi under naturally vegetated soils or grasslands. Replacement of forests with cropland potentially decreases DSi enrichment of base flow towards rivers. It is expected that the concentration of dissolved Si in percolating water will also vary with the retention time of percolating water within the soil. However, this Si enrichment has to our knowledge not been linked to different types of land use.

Within the current project, we focused on the chemical erosion of soil Si in general, as a complement of the experiments towards particulate Si erosion. Subsurface transport will occur through two pathways: the quick through flow (water which flows through the surface soil layer, and reappears at the surface before entering into the river) and the base flow (water reaching the river through the ground water). Suction cups in both forested and agricultural habitat allowed to study the quick through flow and associated DSi concentration changes in the soil, while the continuous sampling of runoff and sediment using a water level logger and a flow-proportional pumping sampler allowed to study both the baseflow and quickflow fluxes of DSi.

Basin-scale survey of Si discharge in sub-basins characterized by different land use

This work package studies the mobilization of Si from a holistic, observational approach. Is the effect of land use on Si fluxes apparent in the rivers draining the sub-basin, characterized by a certain ratio at which landscape types abound? In the Scheldt basin 52 sub-basins were selected of 200+ ha. The sites were chosen to represent all major soil typologies occurring in the Scheldt basin and covered the complete range of land uses occurring in the Scheldt basin. In the selected sub-basins, surface water samples were taken in the draining river, near the location where the river discharges into the higher–order river and water is leaving the sub-basin. Samples within these catchments represent fluxes at base-flow.

Eight stream catchments where arable land use is highly dominant were additionally selected to study erosion fluxes of BSi during rainfall events. Monitoring consisted of continuous precipitation and discharge measurements as well as sampling for suspended matter (SPM) concentration and BSi- and DSi-concentration during peak flow events.

Laboratory DSi/BSi-analysis in vegetation and soil, in subsurface water samples, ground water and sampled sediment

All sediment samples were analysed for ASi content using the sequential alkaline extraction procedure. ASi is extracted from the oven-dried sediment (25 mg) in a 0.1 M Na2CO3 solution at 80°C. Subsamples are taken after 150, 210 and 270 minutes. The extraction solution is then analysed for DSi concentration. ASi content (in $mg.g^{-1}$ dry sediment) is then calculated by extrapolating the linear line through the three extraction points in a time vs. extracted DSi plot. This approach corrects for additional release of Si from mineral silicates. The ASi wet-alkaline extraction is prone to additional release of DSi from amorphous mineral silicates. There are however no alternatives for wet alkaline extraction, especially because the method is also capable of fully dissolving phytolith ASi; despite its flaws, ASi wet-alkaline extraction is for the moment still the most representative method to analyse for ASi.

All water samples and extraction solutions were be analysed for DSi content spectrophotometrically on an IRIS ICP (Inductively coupled Plasma Spectrophotometer).

3. Results and discussion

Sites

52 sub basins were selected differing in land use, drainage efficiency, soil composition and catchment size, along a gradient of landuse, with max 20% urbanization, and excluding catchments where a significant amount of $CaCO_3$ was present in the catchment lithology. These catchments were studied for ASi and DSi fluxes at the sub-basin scale (Fig. 1).

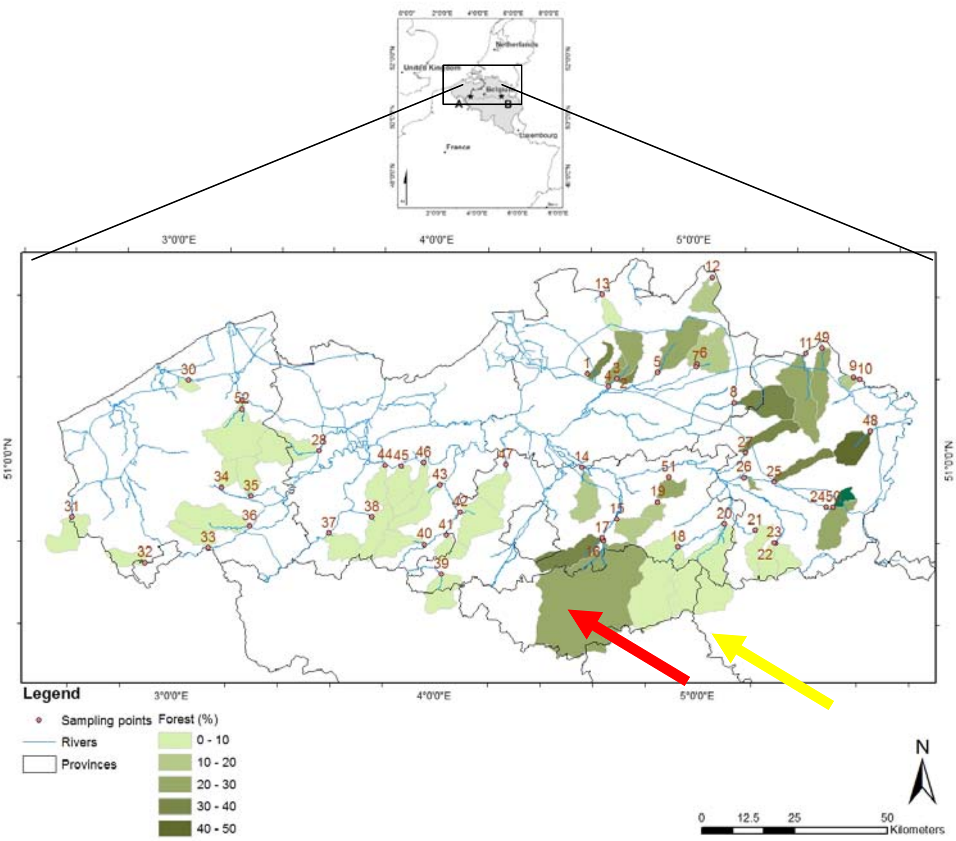


Figure 1: Location of catchments studied for sub-basin scale ASi and DSi fluxes and forestation degree. The location of the Velm (yellow arrow) and the Meerdael and Ganspoel (red arrow) sites, where habitat scale research is performed, are additionally shown.

In addition, 8 permanent sampling stations were selected to study rainfall event related fluxes of DSi and ASi (Figure 2). The catchments are situated in the Southern part of Flanders and are part of two larger sub-basins: the Demer basin (4 catchments with sample stations at Muizen, Velm, Piringen and Wellen) and the Bovenschelde basin (4 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) (Fig. 2).

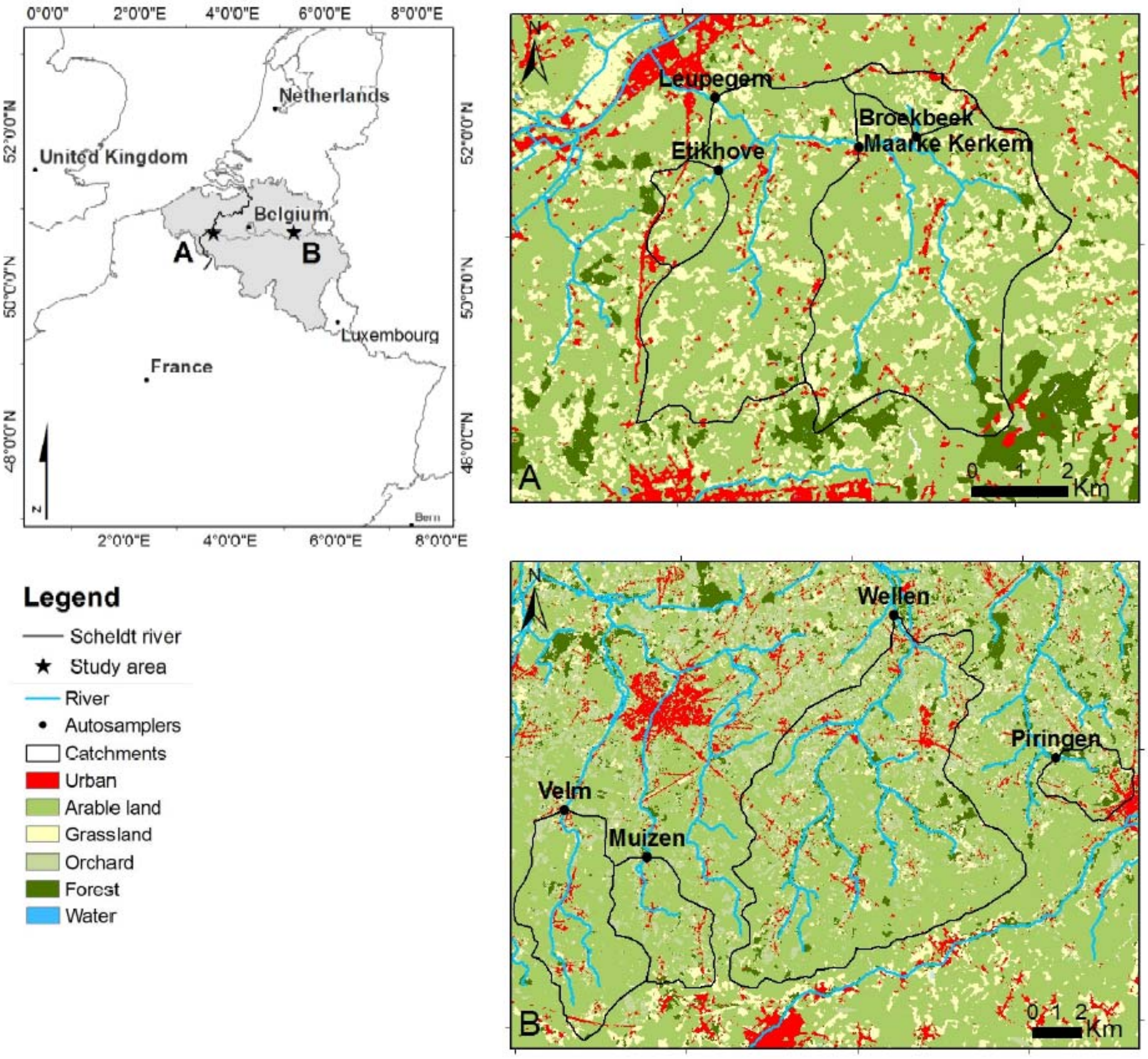


Figure 2: Location of catchments studied for ASi and DSi fluxes during rainfall events.

Mobilisation of Si in arable catchments

Local dynamics

Rainfall experiments

Rainfall simulation experiments were carried out on small plot scale (1 m²) using a well-established protocol on arable land with various crops and with various tillage techniques (winter and summer crops; conventional vs. non-inversion tillage). An overview of the conducted rainfall experiments, in total 130, is given in table 1.

Table 1 Overview of rainfall experiments conducted during the LUSi-project (N=130).

Year	Field	Tillage type[a]	Crop type	N	Sand[b] %	Silt[b] %	Clay[b] %
2008	1VA	CONV, DEE, DD	Wheat	27	34.3	59.1	6.6
	2PE	CONV, DEE	Maïze	6	10.3	80.7	8.9
	6GE	CONV, DEE	Sugarbeet	6	34.3	56.6	9.0
	7VP	CONV, DEE	Sugarbeet	6	47.6	45.0	7.3
	8VP	CONV, DEE	Maïze	4	21.0	69.6	9.5
	10VP	CONV, DEE	Maïze	6	35.7	55.3	9.0
	IWT1	CONV, DEE	Sugarbeet	9	11.0	78.7	10.3
	IWT2	CONV, DEE	Potato	9	11.1	79.4	9.5
	IWT3	CONV, DEE	Potato	6	9.4	80.1	10.5
2009	1VA	CONV, DEE, DD	Maïze	9	34.3	59.7	5.9
	6GE	CONV, DEE	Maïze	6	39.3	52.4	8.3
	10VP	CONV, DEE	Maïze	6	38.1	53.1	8.9
	12LA	CONV, DEE	Wheat	6	25.5	67.2	7.3
	17EV	CONV, DEE	Wheat	6	6.8	80.5	12.7
	IWT2	CONV, DEE	Wheat	6	11.1	79.4	9.5
	IWT5	CONV, DEE	Potato	12	24.5	65.8	9.7

a CONV: conventional plough; DEE: deep non-inversion tillage; DD: direct drilling; b sand (0.063-2mm), silt (0.002-0.063 mm), clay (<0.002mm)

The analysis of the rainfall simulations showed a clear linear relationship ($R^2 > 0.95$) between suspended matter (SPM) and biogenic silica concentrations for the various summer crops (i.e. maize, potato and sugar beet) and tillage types (conventional plough and deep non-inversion).

An ANOVA-analysis of biogenic silica content in the run-off material indicated no significant (sign. level < 0.05) effect of crop ($p > 0.053$) and tillage type ($p > 0.83$). A similar analysis was conducted for dissolved silica concentrations (avg.: 160 ± 85µM, DSi), which were not significantly different for crop type ($p > 0.41$) and tillage type ($p > 0.32$) (Figure 3).

We observed an important relationship between suspended matter concentration and biogenic silica in the run-off. At plot scale these equations make it possible to assess amorphous silica export for summer crops. ASi-losses range between minimum 0 and 80 kg ha^{-1} hr^{-1} but average around 4-6 kg ha^{-1} hr^{-1} while DSi-losses are one magnitude lower with averages around 0.2 kg ha^{-1} hr^{-1} (4% of total Si transport) (Figure 4). On small scale plots ($1m^2$) total silica fluxes were mainly determined by biogenic, amorphous silica fluxes rather than dissolved silica fluxes. Differences in TSi-loss (biogenic + dissolved Si) for experiments were attributed to differences in sediment export. The results confirm that when sediment export is important ASi-loss is equally important, so although there is no significant difference between SPM-ASi relations for crops, there will be a significant difference in BSi-loss for the various crop and tillage types according to the SPM-transport.

Small catchment scale

In the arable catchments, DSi concentration varied between 50-400µM. Fluctuations in DSi concentrations followed fluctuations in discharge. ASi concentration varied between 0-500µM. Concentrations were highly variable within the studied erosion events. A regression analysis showed a clear linear relationship ($R^2 > 0.95$) between suspended particulate matter (SPM) and biogenic, amorphous silica concentrations. The relationship between suspended particle matter and amorphous silica confirms the existence of an important coupling between sediment export and total silica transport in arable catchments. Relative importance of ASi in the total flux varies between 12-55% while DSi varies between 45-88%. DSi concentrations in soil water were slightly higher then those retrieved during peak-events.

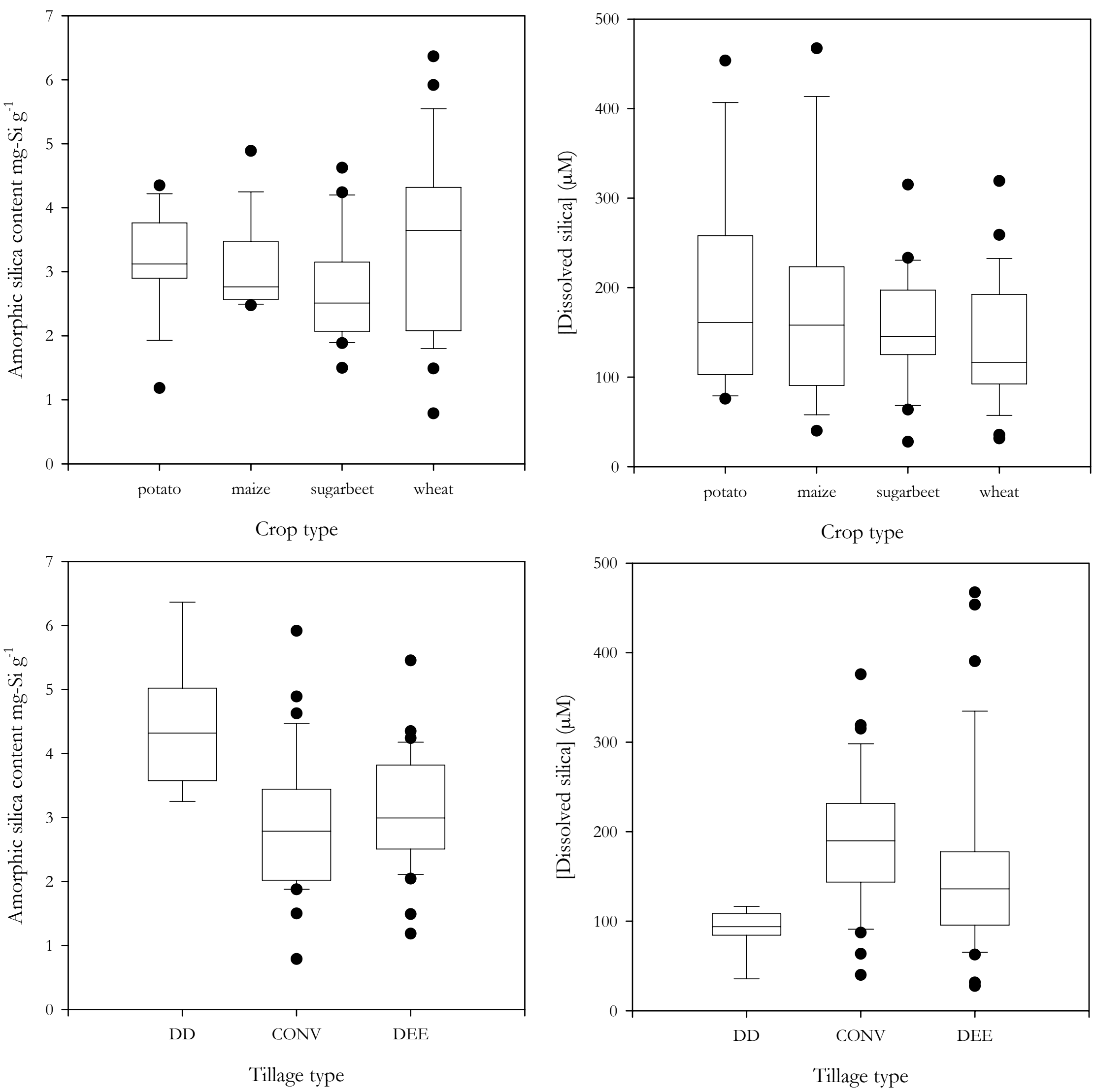


Figure 3 Biogenic, amorphous silica content (mg-Si g^{-1}, left) and dissolved silica concentrations (µM, right) during rainfall simulations for various crop type (top) and tillage type (bottom).

From our agricultural catchment data it is clear that ASi transport is important when erosion occurs. Overland flow is the most important at the beginning of events; subsequently excess overland flow and quick through flow become more important. This is indicated by high SPM and ASi concentration in the beginning of events (Figure 4).

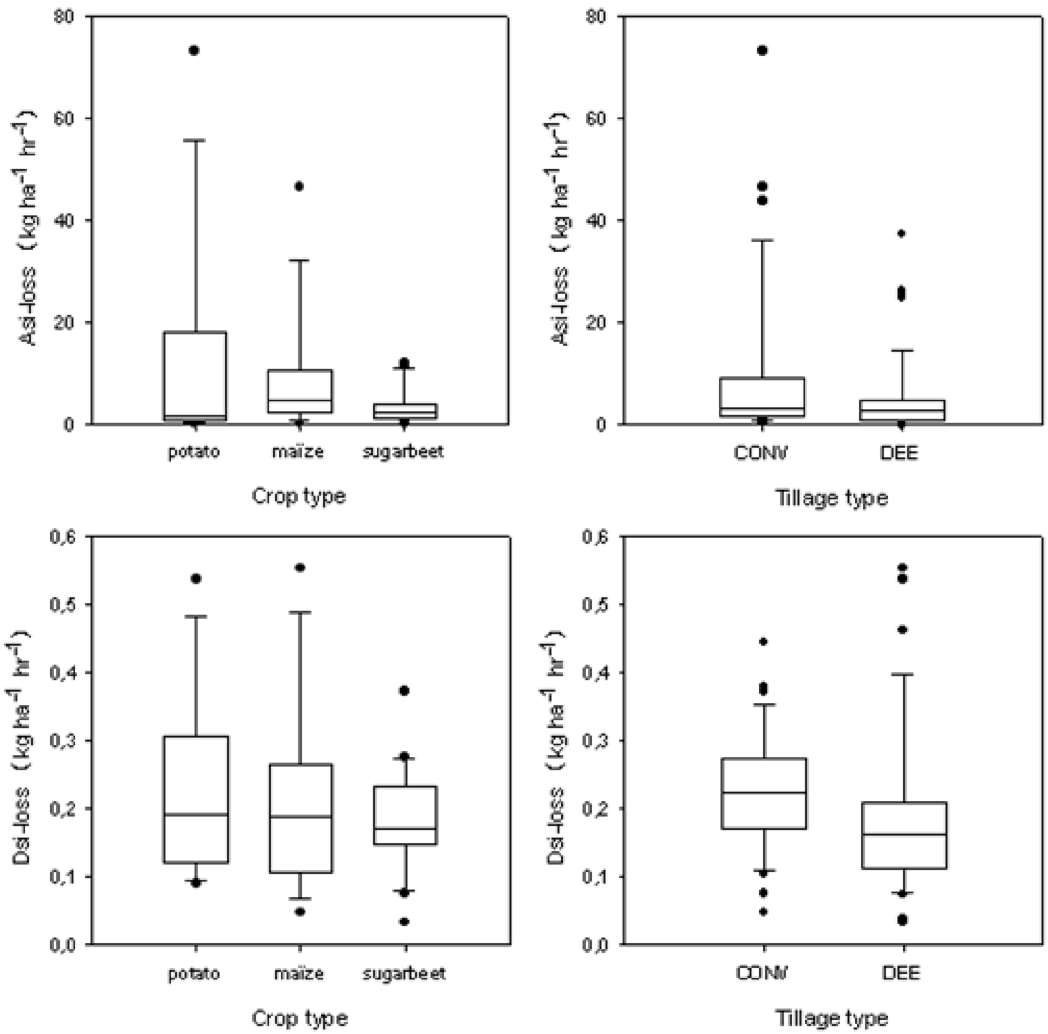


Figure 4: Boxplots for biogenic, amorphous silica losses (kg ha^{-1} hr^{-1}, top) and dissolved silica losses (kg ha^{-1} hr^{-1}, bottom) during rainfall simulations for various crop type (left) and tillage type (right).

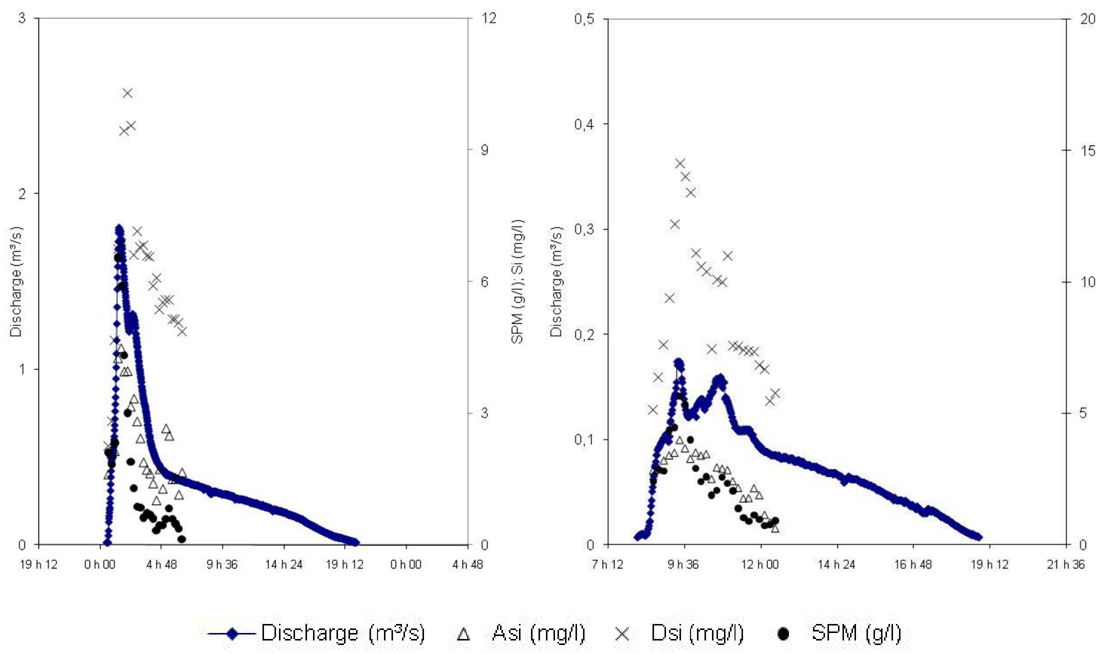


Figure 5: Example of 2 hydrographs at Velm: discharge (m³ s-1), dissolved (cross) (DSi) and biogenic, amorphous silica concentrations (ASi) and SPM.

A trade-off between ASi and DSi

In total, 432 DSi and 330 ASi samples were taken at peak-flow in eight small scale agricultural catchments operated by auto samplers of the Flemish Environmental Agency (VMM), ranging from 14 to 156 samples per catchment, irregularly spread over the period from February 2007 until March 2009.

Generally, DSi concentrations decreased and ASi concentrations increased with increasing discharge (Figure 6). SPM concentration showed a highly significant positive linear correlation with ASi concentration. Where analyzed, the relative amount of ASi increased significantly with the relative amount of organic matter (TOC) in transported SPM.

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 (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.

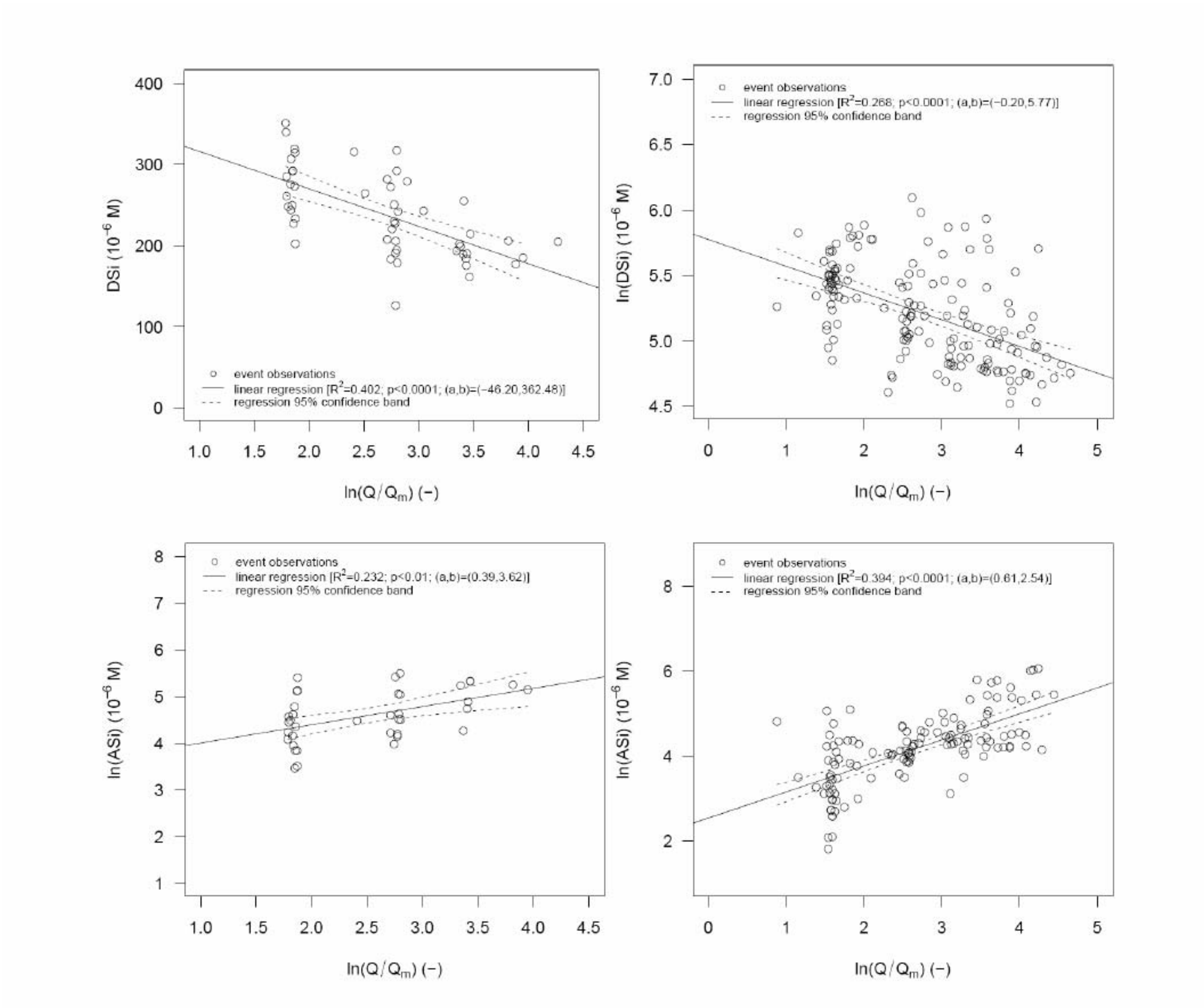


Figure 6: Relations between relative discharge (Q/Qmodal) and DSi - and ASi concentrations in the catchments of Leupegem (left) and Muizen (right). Qmodal is modal discharge from 2006-2008.

On a yearly basis we calculated that 6-40% of all bio-reactive Si was transported as ASi (Table 2). While around 35 to 45% of all water was transported during peak flow events, 68 to 75% of all ASi and 25 to 36% of all DSi was transported at the same time (Table 2).

Table 2 Percentage of the total load of bio-reactive Si (TSi) transported as ASi in all catchments, based on yearly load calculations for 2007. The percentage of DSi and ASi transported during peak events is indicated (PF/TF, peak flow/total 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).

		ASi/TSi (%)			DSi: PF/TF (%)			ASi: PF/TF (%)		
station	r	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

Implications and discussion

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 cropland 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 small events, while this is not the case during large events (Steegen et al., 2001a; 2001b). As ASi is associated with organic matter, the ASi/SPM ratio is expected to decrease with increasing event intensity (towards higher peak discharges) and SPM concentration.

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 (, the ASi concentration (per unit of water) increases with increasing discharge.

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: 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. 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 (. 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. The Scheldt estuary itself is 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). 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 (Conley 2002; Derry et al. 2005; Street-Perrott & Barker 2008; Conley et al. 2008, Struyf & Conley 2009). The physical removal of ASi from surface soil layers might hence also impact buffering of DSi transport through watersheds by ecosystem soils: the effect of this remains poorly studied.

The fate of the mobilized ASi is uncertain: previous research suggests that significant amounts are deposited in wetlands or lakes. 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., 2007). 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.

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. Moreover, the intensity of daily precipitation events is expected to increase. 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% to 12% in the 21st century compared to the 20th 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. Reduced precipitation in summer, and higher drought frequency, 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. 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.

Conclusions

Several questions need focus before we can quantify the importance of the changing 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.

Mobilisation of Si in forested catchments

Local dynamics

A permanent sampling site was installed in Meerdaal forest. The site has similar morphological, geological, geomorphologic and pedologic features as the agricultural sites of Ganspoel and Velm and has a 100% forest cover. For forest overland flow can be neglected, subsurface transport will be the most important. Subsurface transport will occur through two pathways: the quick through flow (water which flows through the surface soil layer, and reappears at the surface before entering into the river) and the base flow (water reaching the river through the ground water).

At base-flow, DSi concentrations varied between 320 – 500 µM for the last 2 years, significantly higher than in agricultural catchments (Figure 7). DSi concentrations are general higher in summer-autumn, ± 450 µM, then in winter-spring, ± 350µM. These seasonal patterns correspond with the variation in occurrence and intensity of precipitation events but also with periods of increased vegetation regeneration.

For peak-flow DSi concentrations decrease rapidly during peak-events followed by a gradual increase of DSi concentrations towards the original equilibrium concentration preceding the event. DSi concentrations vary between base-flow maxima (320 – 500 µM) and reach minima of 70-300 µM.

During base-flow ASi concentration mostly equal 0 but occasionally increase until 150 µM. During peak events ASi concentration usually increase gradually until a maximum of 215 µM, and decrease afterwards. Sometimes a maximum is already reached at the beginning of the event and concentration decrease slowly afterwards. Also for ASi in peak-events maximum values are higher in the summer-autumn period then in the winter-spring period. For some winter-spring events ASi-concentrations remain constantly near to zero although peak flow is occurring.

Monthly suction cup data are available for Meerdaal forest. DSi concentrations are always slightly lower than what we retrieved at base-flow sampling: 250-400µM. No clear seasonal pattern can be distinguished based on these limited sampling points.

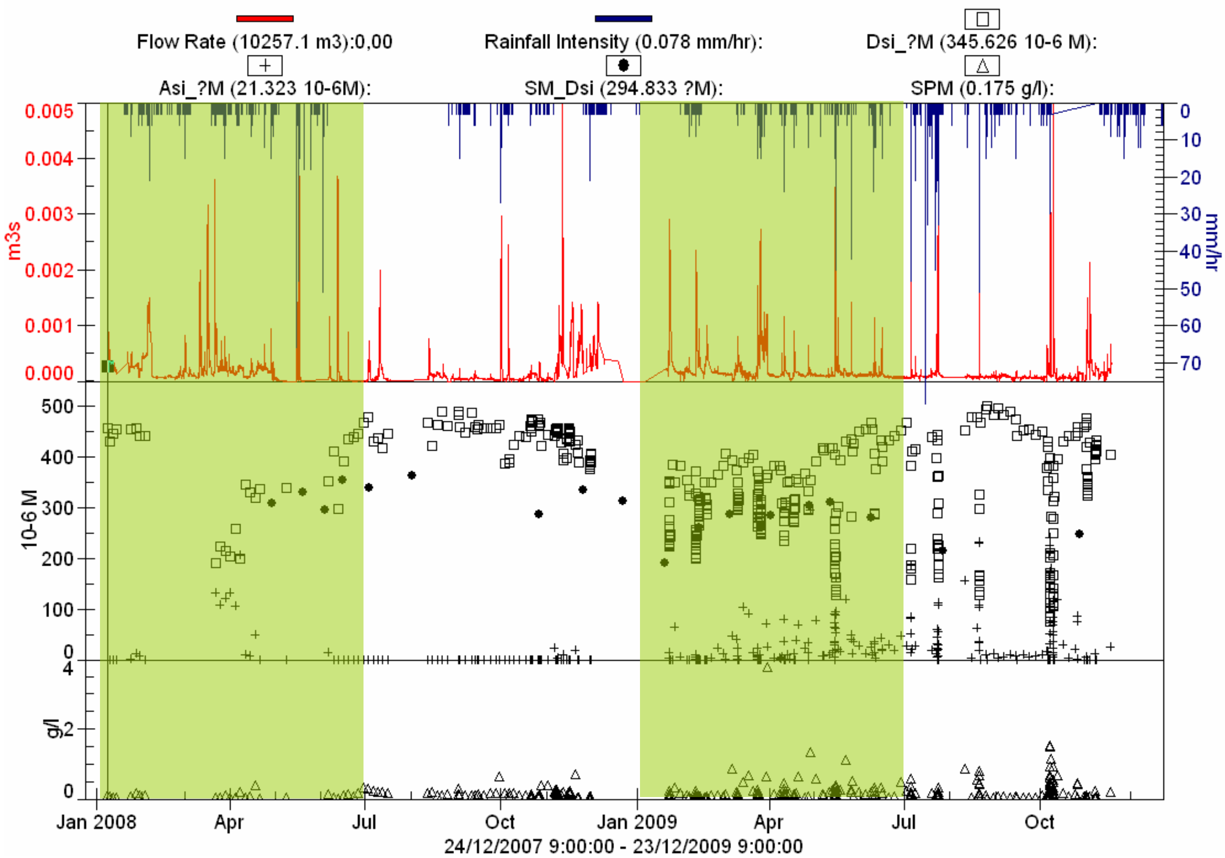


Figure 7 Overview of the gathered data ('08-'09): discharge (red, m³ s^{-1}), rainfall intensity (blue, mm hr^{-1}), dissolved (square) and amorphous silica (cross) concentrations (µM) for river samples, dissolved silica concentrations (solid circles, µM) suction cups and SPM (triangle, g l^{-1}) data.

For base-flow a median ASi concentration of 2µM and DSi concentration of 438µM result in an average TSi concentrations of 440µM with ASi fraction of 0.5% and a DSi fraction of 95.5%. Total Si transport is determined by DSi during base-flow.

It is clear that under forest dissolved silica transport is much more important then amorphous silica transport. This is the case for both base-flow and peak-flow. Only severe peak-events will induce a significant ASi-flux. The most important hydrological pathways under forest are groundwater flow and subsurface quick through flow while overland flow is absent. Higher ASi flux during severe events result from gully bed disturbance. Peak-discharges evoke transport of fine particles and organic material and therefore ASi transport. This low attribution of amorphous silica (0-2%) to the total silica flux is in contrast to what we observe in arable catchments (until 50%). Like for arable land, we observe a dilution-flushing process of dissolved silica during events and wet periods. Our results show that during events and wet periods dissolved silica concentrations undergo an important decrease. This can be explained by the combination of dilution and flushing (Figure 8).

1. During dry periods high DSi concentrations are built-up in the soil pore-water. Soil pore-water reaches the groundwater table through percolation and is transported towards the gully system where high DSi concentrations are measured. A second (unknown) constant flux is recycling by vegetation.

2. The Si in soil pore-water is subject to dilution and flushing during severe rainfall events. Si-poor rain infiltrates and is mixed with Si-enriched pore-water. Due to saturation of the topsoil, a quick through flow depleted in Si arises and further depletes DSi concentrations in the gully. Low DSi concentrations are measured while discharge increases.

3. During a third phase, pore-water becomes enriched in DSi through dissolution of easily available silica. High DSi concentrations are measured as ground water, which remains high in DSi, becomes the main hydrological process again.

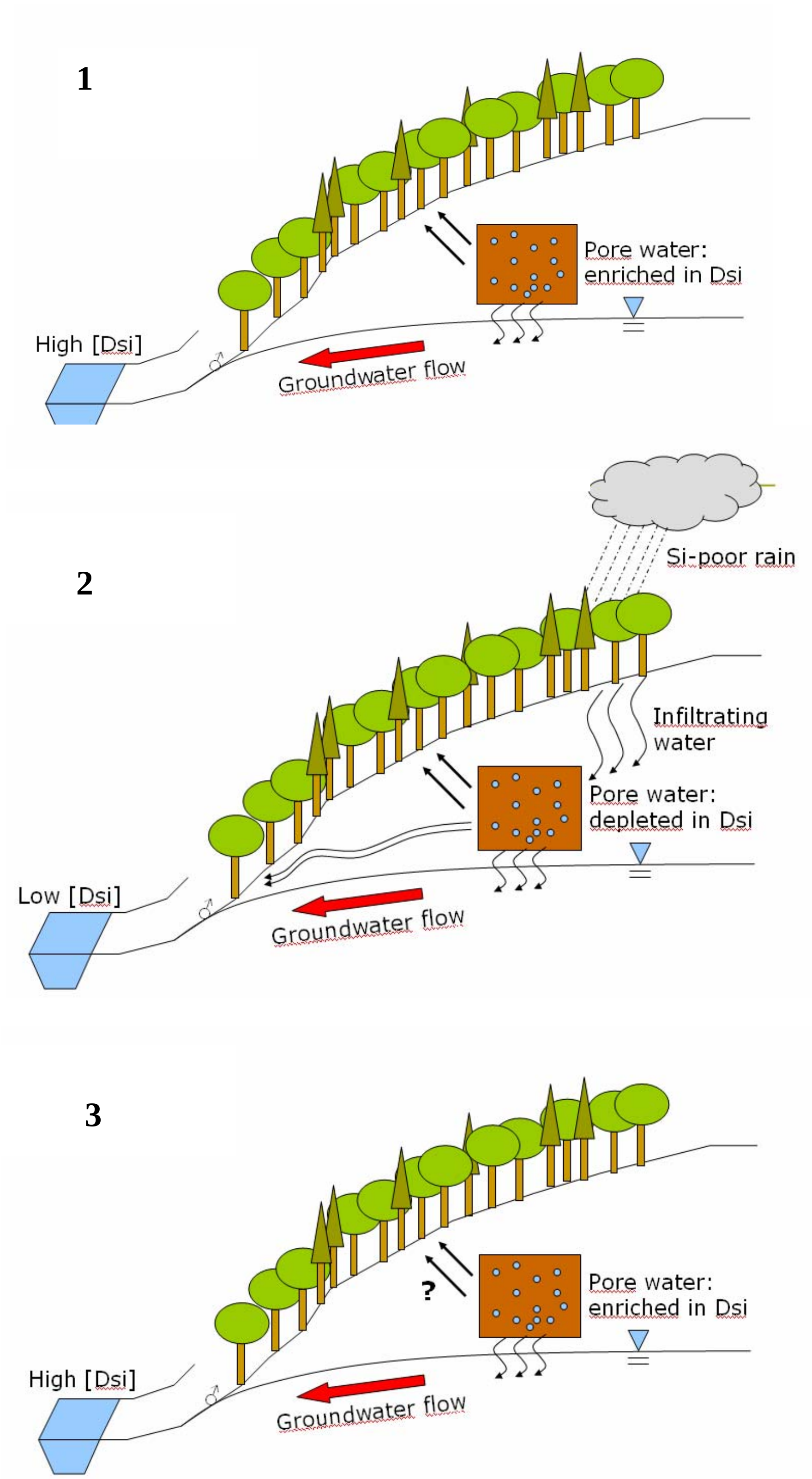


Figure 8: Dilution-flushing effect of DSi during peak-flow events in forested catchments

Effect on catchment scale fluxes of Si

Fifty-one small watersheds were sampled in the Scheldt River basin for base-flow Si fluxes (Table 3). For most of the sampling points, no discharge time series were available. Discharges were compiled from time-series (1971-2008) from nearby gauging stations (<20 km) of the Flemish Environmental Agency (VMM). Topography, land use, soil texture and hydrology of these stations were similar to the studied watersheds. The ratio of instantaneous to long-term mean annual discharge (*Qinst/Qmean)* was assumed to follow a similar temporal pattern throughout the year at the sampling and the nearby gauging location. Combining a simulated long-term mean annual discharge at the location of sampling with the known ratio of *Qinst/Qmean* at the nearby discharge measurement station, allowed to calculate the instantaneous discharge at the sampling location at the time of sampling, as was calibrated and tested for the Scheldt basin. Fluxes were then calculated by multiplying observed Si concentration with calculated instantaneous discharge. Sampling concentrated on small streams, thereby minimising effects of within-stream Si cycling, and was carried out during dry periods so that river discharges were near long-term average baseflow conditions (1971-2008). Our study was therefore representative for typical baseflow conditions in the Scheldt watershed (60-80% of total yearly water flux), with negligible influence of rain-event related dilution and suspended matter mobilization. Benthic diatoms were never observed in any of the sampled streams.

We compared forests to anthropogenic landscape elements (cropland, grassland, urban land) in a space-for-time approach, where gradients in land use in watersheds were considered representative for the effect of long-term land use changes. We carried out a mixed multiple linear regression analysis (MIXED procedure in SAS v.9.2) with the natural logarithm of the total silica flux (ASi + DSi) as the response variable, and three categories of explanatory variables (land use, soil texture and drainage class).

Table 3: Characteristics of the watersheds

	Land cover				Soil texture					Drainage class		
ID	Urban	Grassland	Cropland	Forest	Loam	Clay/Heavy clay	Sandy loam	Light sandy loam	Sand/Loamy sand	1	2	3
1	10.0	20.3	36.1	33.4	0.0	1.9	0.1	4.7	**82.9**	25.3	25.0	38.5
2	10.8	24.6	33.4	31.2	0.0	0.0	0.4	2.8	**87.4**	51.6	16.9	22.1
3	11.3	27.0	33.6	27.2	0.0	1.0	0.5	8.3	**78.4**	20.5	33.7	33.5
4	11.3	27.1	34.7	26.1	0.0	1.2	1.6	7.8	**78.5**	21.8	32.4	34.6
5	17.8	20.4	38.3	22.5	0.0	0.0	0.1	3.6	**72.0**	22.1	25.8	25.8
6	11.3	24.4	**50.8**	13.2	0.0	0.0	0.0	2.0	**86.7**	21.4	26.1	42.8
7	13.5	24.1	**47.2**	14.6	0.0	0.0	0.0	1.1	**82.2**	21.6	24.4	39.6
8	15.9	31.9	21.0	30.5	0.0	0.0	0.0	2.7	**60.5**	25.0	15.4	20.2
9	7.9	30.8	**47.3**	13.2	0.0	0.0	0.0	1.2	**84.1**	21.8	24.2	39.3
10	6.7	31.7	**48.8**	12.1	0.0	0.0	0.0	0.4	**88.4**	17.4	27.5	44.0
11	19.0	26.8	31.5	21.2	0.0	0.0	0.0	0.3	**83.2**	40.2	23.8	14.2
12	6.4	23.7	**50.2**	19.2	0.0	0.0	0.0	3.1	**92.8**	15.0	54.2	26.1
13	10.1	36.4	**49.9**	2.0	0.0	0.0	0.0	21.7	**65.9**	15.1	36.9	35.5
14	12.1	11.7	**64.3**	11.4	45.7	2.7	31.0	2.5	3.9	37.8	26.3	19.2
15	12.7	8.4	**67.6**	10.9	8.9	5.1	**60.4**	2.0	5.7	56.1	11.9	6.5
16	12.4	14.7	**50.8**	20.9	**71.5**	0.2	7.7	0.1	6.3	76.4	3.6	4.6
17	7.1	10.7	**48.8**	32.5	**65.5**	0.3	3.2	0.0	5.4	62.5	4.0	2.6
18	5.8	12.1	**77.8**	3.5	**90.2**	0.3	0.9	0.0	0.2	78.9	6.2	5.7
19	4.5	7.5	**77.1**	10.2	2.4	7.3	**75.9**	0.9	6.8	44.5	28.0	9.9
20	5.6	8.7	**80.8**	2.4	**85.1**	0.7	3.2	0.4	0.2	77.9	5.8	4.3
21	5.5	4.0	**88.4**	2.1	**76.8**	0.7	8.5	0.4	0.1	54.7	22.2	9.6
22	1.5	6.1	**87.2**	5.0	**86.0**	2.1	0.7	0.3	1.1	76.4	5.6	6.8
23	3.0	4.6	**86.6**	5.5	**84.4**	0.8	0.5	0.0	0.1	72.9	3.8	8.4
24	7.7	11.0	**59.7**	20.4	**53.1**	1.9	5.3	1.3	26.4	63.0	12.2	12.3
25	19.2	22.8	22.9	31.5	0.0	0.0	0.0	0.1	**70.9**	35.7	18.5	14.2
26	0.6	**48.5**	21.9	28.1	0.1	2.6	36.8	8.4	46.8	17.3	29.6	49.3
27	20.0	26.0	21.8	31.2	0.0	0.0	0.0	5.0	**65.2**	30.7	21.4	14.8
28	5.4	32.9	**58.9**	2.9	0.0	5.4	41.4	26.2	23.9	32.7	44.8	19.5
29	8.1	33.2	**50.6**	8.0	0.0	4.8	9.8	18.2	**64.3**	32.5	38.9	25.7
31	1.7	12.4	**68.2**	0.8	0.0	8.7	**72.1**	0.4	0.0	2.7	16.1	9.1
32	1.2	19.3	**66.2**	1.3	**74.7**	10.3	3.7	1.2	2.5	6.8	58.9	23.5
33	13.28	17.23	**67.0**	2.49	0.0	4.7	**64.6**	22.5	1.2	18.1	51.4	19.6
34	14.8	15.5	**66.8**	2.7	0.0	1.8	19.7	**54.6**	15.9	33.4	44.4	14.2
35	14.2	18.0	**67.4**	0.3	0.0	6.9	25.2	34.8	23.2	46.0	30.4	16.3
36	18.3	17.6	**63.0**	1.0	0.0	5.4	45.8	32.6	3.4	20.4	47.8	19.0

37	4.0	21.1	**71.4**	3.5	47.7	5.7	37.1	1.7	0.3	50.6	31.8	10.4
38	8.3	21.7	**58.8**	6.6	**73.5**	3.1	6.0	0.0	0.1	52.2	21.1	8.6
39	4.5	27.0	**60.3**	8.0	**94.6**	1.0	0.1	0.0	0.0	35.1	52.7	5.8
40	4.2	27.0	**66.7**	2.2	**83.2**	1.4	5.8	0.0	0.0	57.6	21.1	11.7
41	3.9	28.8	**63.0**	4.3	**53.8**	0.6	35.1	0.0	0.0	70.5	13.7	9.6
42	10.2	20.2	**64.4**	5.1	**71.7**	2.1	17.2	3.9	0.1	71.6	13.7	8.9
43	8.8	26.4	**63.0**	1.7	**83.1**	0.6	2.7	0.0	0.0	63.6	11.8	11.0
44	7.6	20.6	**65.9**	5.7	29.7	1.2	**51.5**	7.0	2.3	39.2	34.5	17.9
45	10.6	18.1	**67.6**	3.5	29.9	0.6	**56.8**	1.8	0.4	39.0	32.4	18.3
46	11.5	23.6	**61.4**	3.4	43.4	1.8	34.4	3.8	0.6	41.9	28.5	13.6
47	9.5	18.1	**69.9**	2.5	**64.5**	1.1	29.7	0.0	0.0	61.1	21.8	12.4
48	16.04	15.21	23.90	44.49	0.0	0.0	0.0	0.5	**80.6**	67.4	4.4	7.1
49	11.97	26.60	35.07	25.74	0.0	0.0	0.0	0.0	**85.7**	49.8	18.3	15.8
50	8.73	18.57	25.63	43.63	0.2	0.4	0.4	0.3	**88.9**	66.2	13.4	10.7
51	3.40	9.21	66.99	20.29	0.0	22.4	36.3	8.3	27.4	30.3	35.5	19.6
52	6.76	32.39	51.46	9.35	0.0	5.2	14.5	17.1	**60.9**	34.9	37.2	25.5

Table 3 Continued	Catchment characteristics				Discharge-weighted average		
	Area	Length	Order	Specific discharge	DSi concentration	ASi concentration	TSi Flux
ID	km^2	m		10^{-4} m^3 s^{-2} km^{-2}	µmol L^{-1}		µmol ha^{-1} s^{-1}
1	23.7	16024	3	115	236	5.3	23.5
2	10.9	8957	2	103	249	5.0	25.0
3	66.3	19650	3	105	267	5.7	27.4
4	85.4	23343	4	113	256	9.2	29.0
5	98.2	22815	4	107	251	9.2	31.1
6	43.9	14174	3	105	184	9.9	17.0
7	98.8	15443	4	104	150	8.6	13.9
8	98.5	22442	4	108	202	6.9	18.5
9	4.7	4773	2	73	276	5.0	21.6
10	13.9	6348	3	79	259	4.5	22.2
11	134.4	28658	3	109	191	5.6	17.4
12	48.7	14116	3	112	223	8.1	49.4
13	31.3	11787	4	114	294	4.3	9.5
14	68.4	21887	4	79	391	4.9	31.3
15	48.2	11264	3	81	403	7.7	26.9
16	641.5	40984	4	92	315	11.4	27.2
17	81.3	22613	3	95	349	6.8	38.7
18	237.8	29936	4	71	301	12.0	19.6
19	23.4	6012	3	80	312	10.0	22.8
20	274.2	33185	3	67	428	20.1	26.1
21	50.5	16770	3	66	452	10.7	28.5
22	40.9	9156	3	77	253	7.1	14.1
23	38.6	12634	3	73	315	6.5	16.3
24	95.2	15343	4	95	222	8.5	21.0
25	42.0	20002	3	111	191	5.4	19.9
26	2.5	8511	2	86	218	3.8	29.5
27	47.5	20879	3	109	213	6.2	17.7
28	106.9	23486	3	81	405	2.3	8.0
29	146.3	23186	4	93	431	6.1	16.8
31	75.2	10596	4	61	198	6.4	4.2
32	37.8	13179	4	61	201	6.8	4.2
33	45.9	14564	4	68	215	7.6	4.9
34	29.8	10456	3	85	322	4.3	8.6
35	51.6	16562	3	86	328	5.0	8.8
36	108.9	28965	4	75	246	6.0	6.0
37	55.1	13150	4	77	442	10.0	15.6
38	73.1	14235	3	76	395	6.0	25.0
39	74.6	10618	4	78	235	3.4	6.2
40	53.7	17091	4	74	272	3.3	3.5
41	34.0	10371	4	74	313	3.2	13.4
42	100.2	16008	4	78	358	4.7	12.2
43	54.4	22324	3	75	319	2.8	49.9
44	42.9	13858	4	77	396	4.9	12.0
45	56.4	14384	4	77	310	12.1	9.5
46	52.7	22433	3	77	259	6.8	7.5
47	55.4	16428	4	78	290	4.0	17.0
48	66.0	14875	2	98	292	2.3	14.4
49	69.0	22389	3	100	157	1.9	12.8
50	19.0	6565	3	111	209	8.4	12.7
51	32.7	9423	3	87	417	4.6	27.4
52	75.2	19509	4	90	450	5.2	6.9

Total biologically reactive silica fluxes (TSi, comprised of amorphous silica (ASi) from phytoliths and diatoms, and dissolved silicate (DSi)) were determined at baseflow in a temperate European watershed with a long agricultural history (> 1000 years). The correlation between successive observations at the same location was 63%. This quantitatively supports our assumption that all observations represent the long-term average baseflow conditions Mean watershed DSi concentrations ranged from 150 µmol L-1 to 485 µmol L-1 while ASi concentrations ranged from 4 µmol L-1 to 15 µmol L-1. Si transport at baseflow was completely dominated by DSi: averaged over the 52 watersheds, the relative contribution of ASi to TSi transport ranged from ~1.5 % during summer months to ~4.5 % during winter and spring months. Only land use (p = 0.0149) had a significant influence on the TSi fluxes. Soil texture (p=0.3279) and drainage class (p=0.1018) had no significant impact. The contrasts 'forest vs. human' (p=0.0214), 'forest vs. agriculture (grassland + cropland)' (p=0.0050), 'forest vs. grassland' (p= 0.0023) and 'forests vs. cropland' (p < 0,001) were all significantly greater than zero (Table 4). The wide two-sided confidence interval for the contrast 'forest vs. urban' indicates genuine uncertainty so that we cannot exclude the possibility that forests lead to a smaller TSi flux compared to urban land use. The results of Bonferroni's multiple comparison procedure to correct for multiple testing strongly support the hypothesis that forested areas have higher TSi fluxes than the other land use types (Table 4).

Contrast estimates (Table 4) from the regression analysis can be used to quantify the observed increase in TSi fluxes with increasing forest cover. The contrast "forest vs. human" (point estimate: 0.02173, Table 4) indicates that 1% of forest cover increase at the expense of a 1% decrease in human land cover results in a factorial increase of TSi flux of e0.02173 (=1.022) or a relative increase of 2.2% of TSi fluxes. Similarly applying all estimated significant contrast from the analysis, the estimated relative increase in TSi flux associated with e.g. a 20% increase in forest cover is between 65 % (if only grassland is replaced) and 25 % (if only cropland is replaced) (Fig. 9). The upper contrast estimates indicate an increase of more than 200% in TSi flux with only 35% increase in forest cover. Confidence intervals clearly point to an overall positive effect of forests on the TSi flux in the sampled rivers (Fig. 1).

Table 4 Results of multiple regression analyses. Upper panel: point estimates, p-values and 95% confidence limits of the point estimates for contrasts comparing the impact of a 1% increase in forested land use on the natural logarithm of TSi flux (µmol.ha-1.s-1) coinciding with a 1% decrease of other land uses. Lower panel: point estimates, p-values and 95% confidence limits corrected using the Bonferroni procedure for multiple comparisons.

Contrast name	Point Estimate	P-value	Two-sided Confidence Interval		One-sided Lower Confidence Limit
Forest vs human	0.02173	0.0214	0.00075	0.04271	0.00417
Forest vs agricultural	0.02344	0.0050	0.00581	0.04108	0.00869
Forest vs. urban	0.01814	0.1913	-0.02296	0.05923	-0.01625
Forest vs pasture	0.03318	0.0023	0.01061	0.05575	0.01429
Forest vs cropland	0.01370	0.0424	-0.00191	0.02932	0.00064

Contrast name	Point Estimate	P-value	Two-sided Confidence Interval		One-sided Lower Confidence Limit
Forest vs human	0.02173	0.1070	-0.00613	0.04959	-0.00333
Forest vs agricultural	0.02344	0.0250	0.00003	0.04686	0.00238
Forest vs. urban	0.01814	0.9565	-0.03644	0.07272	-0.03095
Forest vs pasture	0.03318	0.0115	0.00321	0.06315	0.00623
Forest vs cropland	0.01370	0.2120	-0.00703	0.03444	-0.00494

These results contrast with a previous study from the Hubbard Brook Experimental Forest (HBEF) (Conley et al. 2008) where increased export of DSi was observed up to 20 years after forest harvesting. These increased Si fluxes were partly related to plant materials remaining on the soil surface following deforestation. In addition, mobilization and redistribution of ASi stocks occurred in the forest soils. We hypothesize that the observations should be interpreted as two distinct stages after the cultivation of formerly forested areas (Fig. 10): HBEF is representative for the situation directly after deforestation (< 100 year), the Scheldt watershed is representative for sustained long-term forest soil disturbance (> 200-500 year).

We propose a novel conceptual model where initial forest development is characterised by small amounts of DSi released from the soil ASi pool, compared to the amount that is annually added to the vegetation and to the soil ASi pool. Developing forests form net sinks for DSi: unfortunately, little or no research is currently addressing Si dynamics in developing forests. An equilibrium state will eventually be reached: this stage is characterised by a large, slowly growing soil ASi stock (Cornelis et al. 2010).

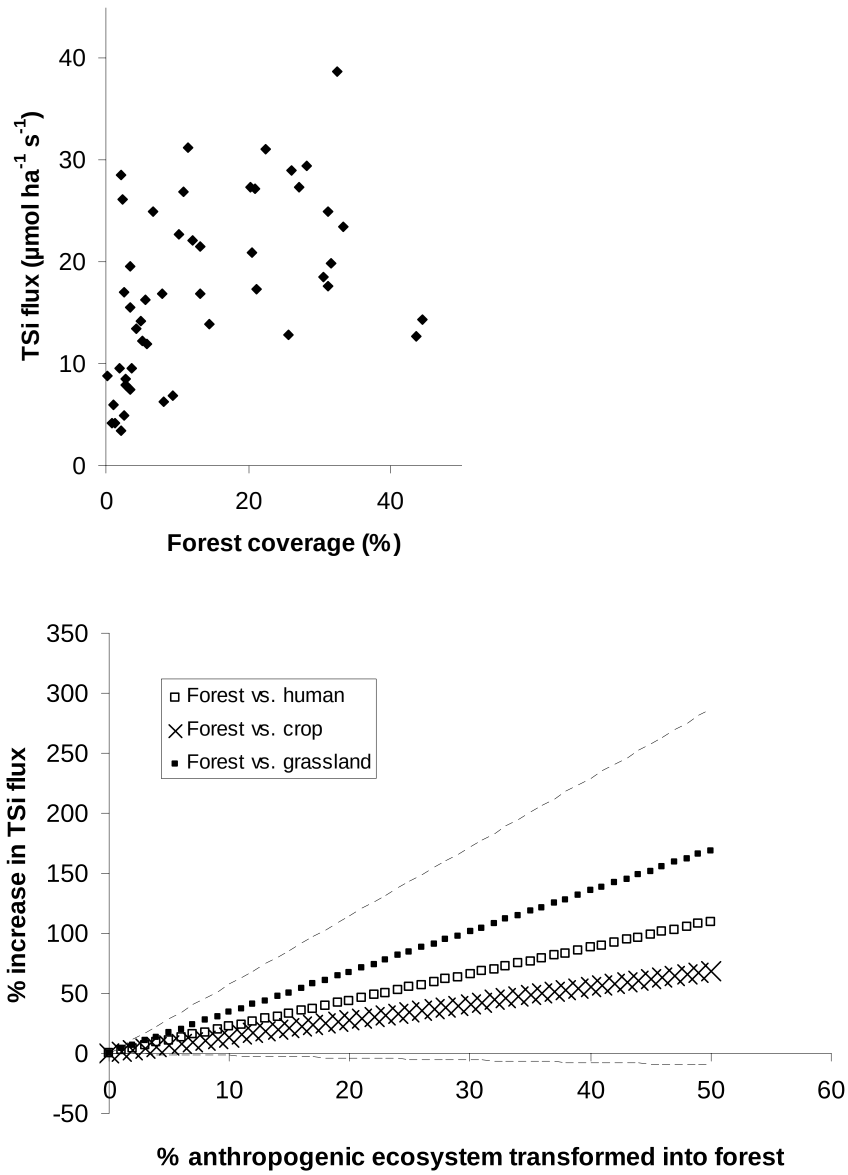
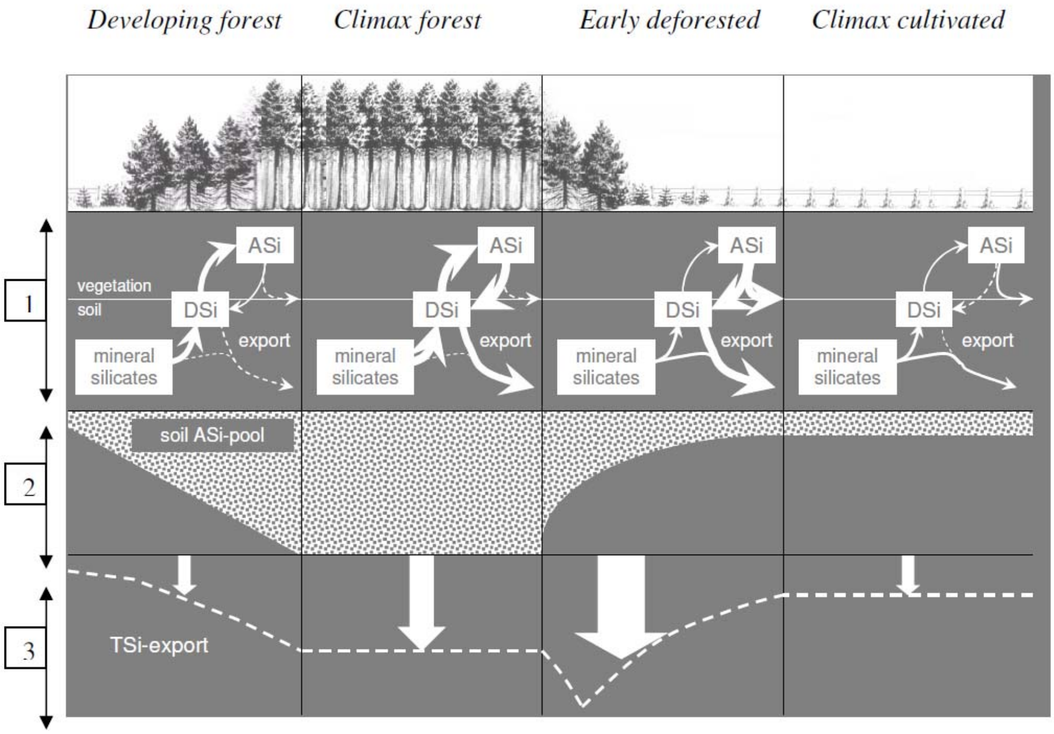


Figure 9: Deforestation and Si fluxes in the Scheldt watershed. Upper panel: variation of TSi flux (averaged per watershed) with forest cover. Lower panel: percentage increase in TSi flux coinciding with % increase in forest cover, as estimated from the mixed multiple linear regression analysis. The three contrasts represent the point estimates, the dashed upper and lower line represent the upper (from forest vs. grassland) and lower confidence interval (from forest vs. crop).

The forest vegetation stimulates bedrock weathering of silicates through increases in soil CO2 content, production of organic acids and stabilization of organic soil cover. Trees take up the weathered dissolved Si (DSi) and deposit it as ASi plant-bodies (phytoliths) in their biomass. The major part of the weathered DSi passes through biomass before it is eventually released to rivers. The eventual export fluxes of Si from the climax forest soils are controlled by the dissolution of soil phytoliths. With deforestation, the amount of DSi exported from the forest soils drastically increases as ASi stocks dissolve. However, DSi fluxes may be expected to gradually decrease again over time as there will be a fundamental imbalance: the production of biogenic ASi no longer balances the total amount of ASi dissolved, as harvesting of crops prevents replenishment of the soil ASi stock. Soil erosion will increase and ASi will be physically removed from the soils, especially during precipitation events. Increased TSi fluxes will only last until the soil reaches a new climax cultivation state, characterised by lower export TSi fluxes. The absence of deep-rooting vegetation and the absence of a significant soil organic layer restrain vegetation stimulated weathering mechanisms.

The timescale during which increases in TSi fluxes can be expected after forest cutting is currently not possible to estimate. In the HBEF enhanced export of DSi is occurring 20 years after harvesting of the forest. About 16 kg DSi y-1 ha-1 was exported from the HBEF deforested watershed, although the estimated total soil ASi pool in the integrated soil profile was about 17000 kg ha-1. This already suggests that the increased Si flux could be sustained over ca. 1000 yrs. Moreover, the upper soil layer (O horizon) on its own contained only about 2000 kg ha-1, which could be depleted in about 125 years. The depletion of the ASi stocks in the lower soil horizons will likely be incomplete: several mechanisms inhibit ASi mobilisation in deeper soil layers, including reprecipitation in secondary mineral silicates (e.g. allophanes, immogolite, kaolinite) and incorporation of Al in phytoliths, rendering them less soluble. If forest is converted to arable land, soil erosion will also remove ASi through physical erosion, thereby further reducing the timeframe during which increased DSi export can be expected.

Figure 2 New conceptual model for changes in Si cycling with long-term soil disturbance. (1) Hypothesised Si cycling in developing forest, climax forest, early deforested areas and equilibrium cultured areas, the associated soil ASi stock (2) and the resultant magnitude of TSi export (3). In (1), boxes represent stocks of Si. Arrows represent fluxes: the thickness of arrows is representative for flux size. Dashed arrows represent irrelevant fluxes. In (2), the dotted area represents the size of the soil ASi pool. In (3) the sizes of the arrows represent relative TSi fluxes. The dashed line represents the hypothesized evolution of the size of the TSi fluxes.



The Scheldt watershed has been one of the most densely populated areas in Europe already since the 13th century. As early as 1250, only 10% woodland cover was left (Tack & Hermy 1998); in a pristine state the Scheldt watershed was almost fully forested (>90 %). In this conceptual model, the present Scheldt watershed therefore represents a new equilibrium state, which arises after forest soil ASi has been depleted or immobilised

Grasslands and croplands behave similarly in our dataset. Grasses are known to accumulate significant amounts of ASi, resulting in the presence of a large phytolith pool in soils1.Yet, in our study, the grasslands were not observed to increase the downstream DSi flux. Other authors point to large phytolith stability in soils dominated by grasses (Kelly et al. 1998). This might indicate a gradual dissolution of phytoliths in forest, and a more stable phytoliths pool in grasslands. Another explanation for low DSi fluxes from the Scheldt watershed grasslands is their intense management. The grasslands studied in other studies1 consisted of natural short grass steppe and mixed and tall grass prairie communities. Such natural and semi-natural grasslands cover only 0.3% to 0.6% of the Scheldt watershed. The majority of the grassland is grazed intensively and/or mown several times per year (pastures). Furthermore, pastures are often converted to cropland within a crop rotation scheme of 3-4 years. Grazing and mowing of grasslands result in a large "anthropogenic export" of phytoliths, and the temporary cropland stage (with increased erosion) neutralizes the positive effect of pastures on ASi accumulation.

Recently established forests in Flanders often consist of conifers (pine). Acid soil conditions found in coniferous forests could increase DSi fluxes through increased weathering, but also decrease DSi fluxes from reduced ASi dissolution under acid conditions. Thus, the current state of forests in Belgium is not representative for the deciduous climax forest. Another complicating factor could be the preferential reforestation on sandy soils, exhibiting higher drainage efficiency than loamy soils. However, our data showed no evidence that drainage capacity had a significant impact on the observed TSi fluxes.

Despite these unknowns, and the uncertainty associated with the timeframes in the conceptual model, our data still clearly indicate that long-term soil disturbance and a millennium of agricultural development has strongly changed biogeochemical Si dynamics in the Scheldt River Basin (which represents a good example of long-term cultivation of temperate European watersheds). Modern agricultural practices also result in increased input of N and P into the aquatic continuum, resulting in Si limitation in aquatic ecosystems, with potentially negative effects on ecosystem quality. Our new hypothesis suggests DSi limitation in the adjacent aquatic systems could be counteracted initially by increased Si export from cultivation of former forest soils. As the soil ASi pool gradually declines, this counter-effect diminishes and Si mobilization becomes lower compared to pristine conditions. This view implies that Si depletion events in more recently cultivated areas could currently still be masked by increased DSi export fluxes from recyclable ASi pools. In the Scheldt watershed, lowered Si fluxes were already attained long before intense fertilization started, and no such masking was observed.

Our results emphasize the necessity of increasing our understanding of land use impacts on biogeochemical Si cycling, with a millennium of soil disturbance after deforestation leading to 2-fold to even 3-fold decreases in TSi flux from a watershed where the adjacent coastal zone has experienced significant coastal eutrophication problems due to changes in Si/P and Si/N river deliveries in the three last decades. Our results emphasize that locally factors controlling terrestrial Si mobilization can be refined differently from factors important at continental and global scales, where controls mostly include lithology, precipitation and slope. We clearly show that land use should be included in watershed scale models for base-line silica mobilization. Our results shed new light on how historical cultivation has affected the terrestrial silica cycle, and indicate yet another anthropogenic reduction of silica fluxes through the aquatic continuum, adding to globally important reductions in riverine Si transport by deposition in reservoirs and in eutrophied rivers and estuarine sediments. To refine our concept of land use changes and silica dynamics, determination of germanium/silicon ratios5 and the analysis of the isotopic Si composition of the river water can be used to trace the source of riverine DSi. As such, these techniques may provide additional evidence for the differences in terrestrial biological control between forested and cultivated catchments.

4. Recommendations and future prospects

Recommendations

It has been demonstrated in the project that silica release from land should be incorporated in the eutrophication debate. Our results indeed have added a new factor in integrated water management. This project contributes to decision support in following ways:

- Incorporation of our findings in models can improve their quality with respect to eutrophication in rivers and the coastal zone. As such, organizations such as OSPAR and the EU in general can benefit from our results.
- Implementation of the Water Framework Directive will benefit from this project as the effect of land use on Si can be used in the construction of reference conditions, and in the determination of a classification that also takes Si into account. The results can also have an impact on Conservation Objectives, as silica cycling was imbedded in the construction of conservation objectives of certain habitats such as tidal marshes.
- Measures to reduce erosion, also will change Si delivery to aquatic systems. The project will provide knowledge to link these two aspects. Reforestation has an effect on Si storage. As such, the effect of reforestation of changing nutrient ratios can be evaluated.
- Our observations showed the importance of land use and land cover as regulating factors of riverine Si transport, both ASi and DSi. However, far more additional research is needed to quantify this influence both at base and peak flow.

Future prospects (phase 2)

At base flow, comparative studies in catchments with uniform land use and soil texture will support or refine our hypotheses. In the case of non-uniform catchments, incorporation of the spatial distribution of the different land uses in the catchment may be needed as well. The use of new analytical techniques may support the observed patterns. The determination of germanium/silicon ratios and the analysis of the isotopical Si composition of the river water can both be used to trace the source of riverine DSi and is planned in phase 2. These techniques can give the crucial evidence for the differences in terrestrial biological control between forested and cultivated catchments.

Future research has to reveal more information on the in-stream path followed by the mobilized ASi. Suspended sediments at base and peak flow need to be analysed on ASi from the small headwater streams to the larger stream segments near the estuary, and the presence of terrestrial ASi in river sediments has to be assessed. In combination with the determination of the physical characteristics of the soil ASi pool and the mobilized ASi, this information may allow the incorporation of ASi in erosion and sediment transport models. In these models, a distinction between phytogenic ASi (phytoliths) and mineral ASi phases, which originated by intense ploughing of highly cultivated soils, will probably be needed. To address these topics, during the second phase, we will start to implement a new continuous extraction method that allows to define different reactivity phase within the ASi mobilized.

5. References

Billen G, Lancelot C, Meybeck M (1991) N, P and Si retention along the aquatic continuum from land to the ocean. In: Mantoura RFC, Martin J-M, Wollast R (eds) Ocean margin processes in global change, pp 19-44, Wiley-Interscience, New York

Blecker SW, McCulley RL, Chadwick OA et al (2006) Biologic cycling of silica across a grassland bioclimosequence. Global Biogeochem Cy 20: GB3023.Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochemical Cycles 16: 1121

Cloern JE 2001. Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology Progress Series, 210, 223-253.

Conley DJ, Likens GE, Buso DC et al (2008) Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. Global Change Biol 14: 2548-2554.Costanza R, et al. 1997. The value of the world's ecosystem services and natural capital. Nature 387, 253-260.

Cornelis J.T. , J. Ranger, A. Iserentant, B. Delvaux (2010) Tree species impact the terrestrial cycle of silicon through various uptakes. Biogeochemistry 97, 231-245

Derry LA, Kurtz AC, Ziegler K et al (2005) Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature 433: 728-731.Ducrotoy J-P, Elliott M, De Jonge VN (2000) The North Sea. Marine Pollution Bulletin 41: 5-23

Justic D, Rabalais NN, Turner RE, Dortch Q (1995) Changes in nutrient structure of river-dominated coastal waters: nutrient balance and its consequences. Estuarine, Coastal and Shelf Science 40: 339-356

Kelly E.F, O.A. Chadwick, T.E. Hilinski (1998) The effect of plants on mineral weathering. Biogeochemistry 42, 21-53

Lancelot C (1995) The mucilage phenomenon in the continental coastal waters of the North-Sea. Science of the Total Environmont 165 : 83-102.

Raven JA (2003) Cycling silicon – the role of accumulation in plants. New Phytologist, 158, 419-421

Redfield AC (1958) The biological control of chemical factors in the environment. American Scientist 46: 205-221

Schelske CL, Stoermer EF, Conley DJ, Robbins JA, Glover RM (1983) Early eutrophication in the lower Great Lakes: new evidence from biogenic silica in sediments. Science 222: 320-322.

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, Temmerman S., Meire P (2007) Dynamics of biogenic Si in freshwater tidal marshes: Si regeneration and retention in marsh sediments (Scheldt estuary). Biogeochemistry 82: 41-53. Struyf E, Conley DJ (2009) Silica: an essential nutrient in wetland biogeochemistry. Front Ecol Environ 7: 88-94.

Sullivan MJ, Moncreiff CA (1990) Edaphic algae are an important component of salt marsh food webs: evidence from multiple stable isotope analyses. Marine Ecology Progress Series 62: 149-159

Tack G., M. Hermy (1998) Historical ecology of woodlands in Flanders, in History of European Forests, K. J. Kirby, C. Watkins, Eds. (Cab Int, Wallingford, UK, 1998), pp. 283-292.

Verlaan PAJ (2000) Marine vs. fluvial bottom mud in the Scheldt Estuary. Est Coast Shelf Sci 50: 627-638.

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.

English summary

Background

Nutrient concentrations in the North Sea and adjacent estuaries are the end-result of basin-wide input, retention, mobilization and transport of N, P and Si. Traditionally, eutrophication has been approached as a problem of increased human inputs of N and P. In contrast, dissolved Si concentrations have mostly been considered as not anthropogenically influenced. Transfer of dissolved Si (DSi) to rivers has usually been considered to result from a pure geochemical process, involving only direct chemical weathering of soil minerals. As such, the DSi emission from terrestrial systems affected by human activities into water bodies has been considered relatively constant compared to pristine natural systems. Uptake by diatoms in the river continuum was the main factor used to explain DSi profile changes through time. Current research has clearly pointed out that vegetation cover can have a strong impact on the fluxes of Si through terrestrial ecosystems. It has become clear that ecosystems can store a large amount of Si as amorphous, biogenic Si (amorphous SiO_2nH_2O, ASi), both in soil and vegetation. ASi is far more soluble than mineral Si, and terrestrial Si fluxes are thus potentially strongly controlled by biota. As a result, land use changes and concurrent changes in vegetation cover, have a strong potential impact on the fluxes of Si through river basins.

Still, the release of DSi from different terrestrial systems in river basins has never before been quantified with respect to land use changes. Current knowledge is insufficient to quantify how land use change might have influenced the transport of Si through river basins towards the coastal zone. Such information is however essential for our understanding of eutrophication problems from the upstream aquatic ecosystems way down to the North Sea. As the release of DSi counteracts eutrophication effects, quantifying the role of land use on its emission can lead to a revision of water quality objectives and maintenance objectives. In fact, the history of DSi-emission may have influenced the carrying capacity for primary production much more than is shown by current ecological models. Here lies the relevance of this study.

Objectives

This project aims to answer the question if Si fluxes through a river basin, and ultimately towards the sea, can change because of land use changes. These changes will be budgeted for the Scheldt basin, taking into account surface runoff, subsurface drainage and storage and cycling through vegetation. The results will be used to evaluate the effect of land use changes over historical times on Si fluxes. Moreover, it is the aim to formulate recommendations towards land planning with respect to the reduction of eutrophication, working from the viewpoint of Si in the nutrient ratios. As such, this study of Si can provide a mirror image for the N and P side of the eutrophication problem, and provide invaluable, new insights in our evolving concept of eutrophication

Habitat scale research towards surface erosion and subsurface transport of dissolved Si and amorphous Si and sediments (as an indicator for transport of mineral Si) will be conducted in different landscape types. On a Scheldt basin scale scale, rivers draining sub-basins, will be sampled on a regular basis for all ASi and DSi. The sampled sub-basins will represent a gradient from still largely forested to largely covered by cropland. The integration of results from both site-specific experiments and basin scale sampling will for the first time allow an estimate, based on both historical and recent land use maps, of the extent to which Si fluxes towards the coastal zone have been altered by human land use, and how this change has been triggered by changes in erosion processes, changes in vegetation type and cover, and hydrology.

Results and discussion

Our habitat and small catchment scale research shows that in agricultural catchments ASi is an important component of total Si fluxes, which is in contrast to forested catchments. Transport of ASi mostly occurs during rainfall events. Erosion induces a significant mobilization of topsoil and hence ASi from cropland ecosystems. 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 in croplands.

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: 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. 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. 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. Recent research has emphasized the importance of these ASi rich surface soils as buffers in terrestrial Si biogeochemistry. The physical removal of ASi from surface soil layers might hence also impact buffering of DSi transport through watersheds by ecosystem soils: the effect of this remains poorly studied.

This is apparent from our Scheldt basin scale research towards silica fluxes at base-flow. Based on our results, we propose a novel conceptual model for Si fluxes with deforestation. Initial forest development is characterised by small amounts of DSi released from the soil ASi pool, compared to the amount that is annually added to the vegetation and to the soil ASi pool. Developing forests form net sinks for DSi: unfortunately, little or no research is currently addressing Si dynamics in developing forests. An equilibrium state will eventually be reached: this stage is characterised by a large, slowly growing soil ASi stock.

The forest vegetation stimulates bedrock weathering of silicates through increases in soil CO2 content, production of organic acids and stabilization of organic soil cover. Trees take up the weathered dissolved Si (DSi) and deposit it as ASi plant-bodies (phytoliths) in their biomass. The major part of the weathered DSi passes through biomass before it is eventually released to rivers. The eventual export fluxes of Si from the climax forest soils are controlled by the dissolution of soil phytoliths. With deforestation, the amount of DSi exported from the forest soils drastically increases as ASi stocks dissolve. However, DSi fluxes may be expected to gradually decrease again over time as there will be a fundamental imbalance: the production of biogenic ASi no longer balances the total amount of ASi dissolved, as harvesting of crops prevents replenishment of the soil ASi stock. Soil erosion will increase and ASi will be physically removed from the soils, especially during precipitation events. Increased TSi fluxes will only last until the soil reaches a new climax cultivation state, characterised by lower export TSi fluxes. The absence of deep-rooting vegetation and the absence of a significant soil organic layer restrain vegetation stimulated weathering mechanisms.

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