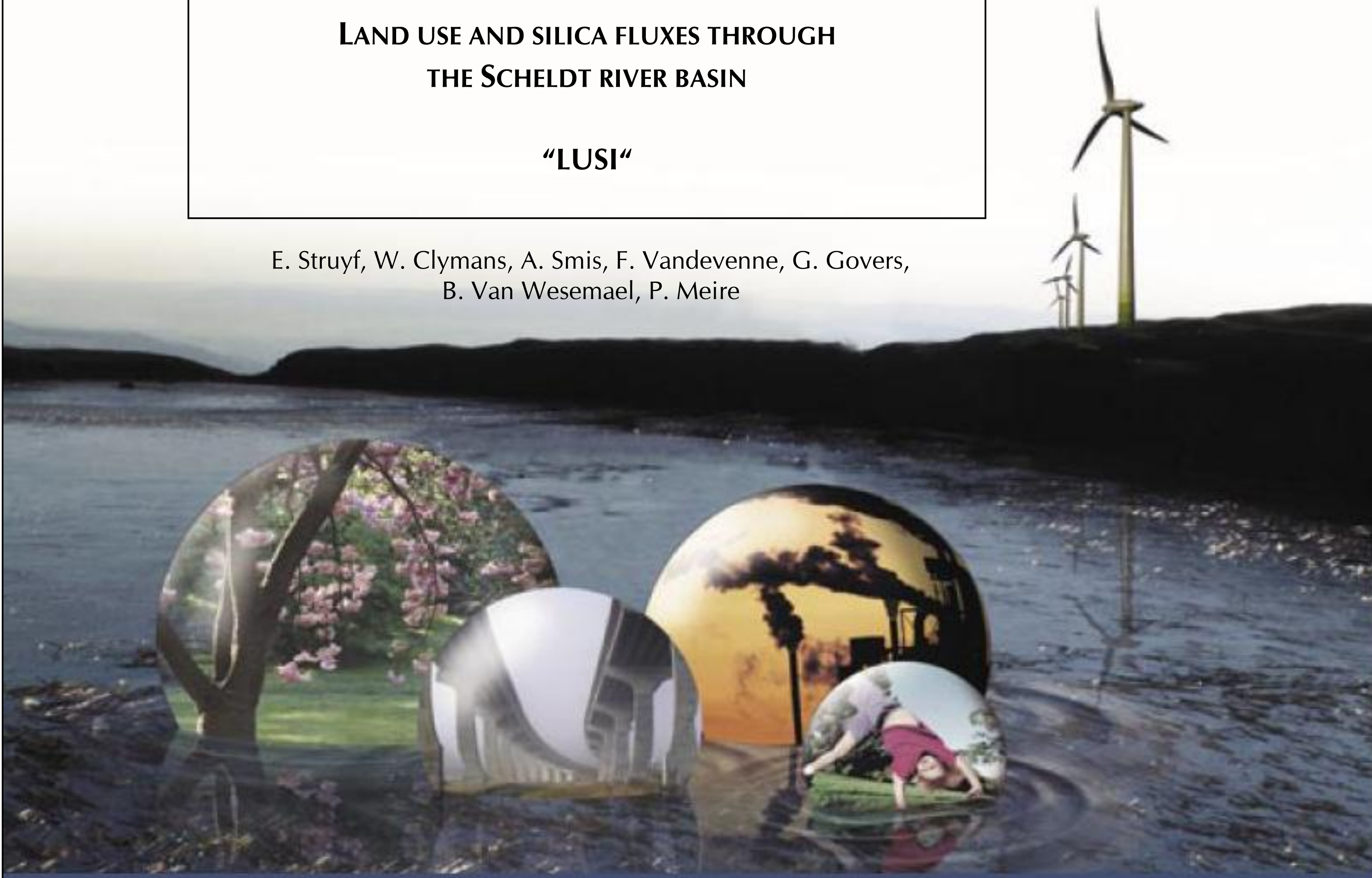
SSD
SCIENCE FOR A SUSTAINABLE DEVELOPMENT

LAND USE AND SILICA FLUXES THROUGH THE SCHELDT RIVER BASIN

"LUSI"

E. Struyf, W. Clymans, A. Smis, F. Vandevenne, G. Govers,
B. Van Wesemael, P. Meire



ENERGY
TRANSPORT AND MOBILITY
AGRO-FOOD
HEALTH AND ENVIRONMENT
CLIMATE
BIODIVERSITY
ATMOSPHERE AND TERRESTRIAL AND MARINE ECOSYSTEMS
TRANSVERSAL ACTIONS

.be

SCIENCE FOR A SUSTAINABLE DEVELOPMENT
(SSD)

FINAL REPORT

LAND USE AND SILICA FLUXES THROUGH THE SCHELDT RIVER BASIN

"LUSI"

SD/NS/05

Promotors
Patrick Meire
Universiteit Antwerpen (UA)
Departement Biologie, Ecosysteembeheer
Middelheimlaan 1
2020 Antwerpen, Belgium

Gerard Govers
Katholieke Universiteit Leuven (KULeuven)
Department of Earth and Environmental Sciences,
Celestijnenlaan 200 E,
Heverlee B-3001, Belgium.

Bas Van Wesemael
Université catholique de Louvain (UCL)
Georges Lemaître Centre for Earth and Climate Research
Earth and Life Institute, Place Louis Pasteur 3,
Louvain-la-Neuve 1348, Belgium.

Authors
Struyf E., Clymans W., Smis A., Vandevenne F., Govers G., Van Wesemael B. and Meire P.

D/2011/1191/35
Published in 2011 by the Belgian Science Policy Office
Avenue Louise 231
Louizalaan 231
B-1050 Brussels
Belgium
Tel: +32 (0)2 238 34 11 – Fax: +32 (0)2 230 59 12
http://www.belspo.be

Contact person: David Cox
+32 (0)2 238 34 03

Struyf E., Clymans W., Smis A., Vandevenne F., Govers G., Van Wesemael B. and Meire P. - ***Land use and silica fluxes through the Scheldt river basin "LUSI ".*** Final Report. Brussels : Belgian Science Policy Office 2011 – 89 p. (Research Programme Science for a Sustainable Development

Table of contents

1. Summary

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 SiO2nH2O, BSi), both in soil and vegetation. BSi 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.

Objectives

This project aimed 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 were 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.

Results and discussion

Our habitat and small catchment scale research shows that in agricultural catchments BSi is an important component of total Si fluxes, which is in contrast to forested catchments. Transport of BSi mostly occurs during rainfall events. Erosion induces a significant mobilization of topsoil and hence BSi from cropland ecosystems. During peak events, a clear trade-off existed between DSi and BSi concentrations, and BSi often became the dominant form of transported bio-reactive Si in croplands.

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 BSi pool, compared to the amount that is annually added to the vegetation and to the soil BSi 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 BSi 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 BSi 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 BSi 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 BSi no longer balances the total amount of ASi dissolved, as harvesting of crops prevents replenishment of the soil BSi stock. Soil erosion will increase and BSi 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.

Our results proof that worldwide massive agricultural Si harvest, and in- and export of food from countries, are reducing potential bio-control and bio-stimulation mechanisms in river basins worldwide. The agricultural silicon harvest is thus a new and important loop in the silica cycle, and its sink function adds and potentially exceeds other important anthropogenically created Si sinks, such as BSi deposition in lakes and reservoirs and reduced weathering stimulation after deforestation. We strongly recommend to start research focusing on this new loop in biogeochemical Si cycling, by the detailed life cycle assessment of harvested BSi, and research focusing on soil Si depletion and biogeochemical consequences in agricultural river basins worldwide.

Finally, we have also made distinct advances in our knowledge of techniques to analyze for BSi in soils and suspended sediments. We have found threshold concentrations where traditional alkaline extraction methods are applicable for terrestrial soils, and are developing novel continuous extraction techniques to gain better insight in lithological interference and reactivity of BSi. We also tested the conceptual model by studying land use and Si fluxes in land use age gradients (in cooperation with Lund University, Sweden) in Southern-Sweden. The age gradients in land use studied here indicated that our conceptual model holds true in other environments. Finally, we summarized current understanding of the effect of ecosystems on terrestrial Si fluxes in a set of scientific recommendations for the future.

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.

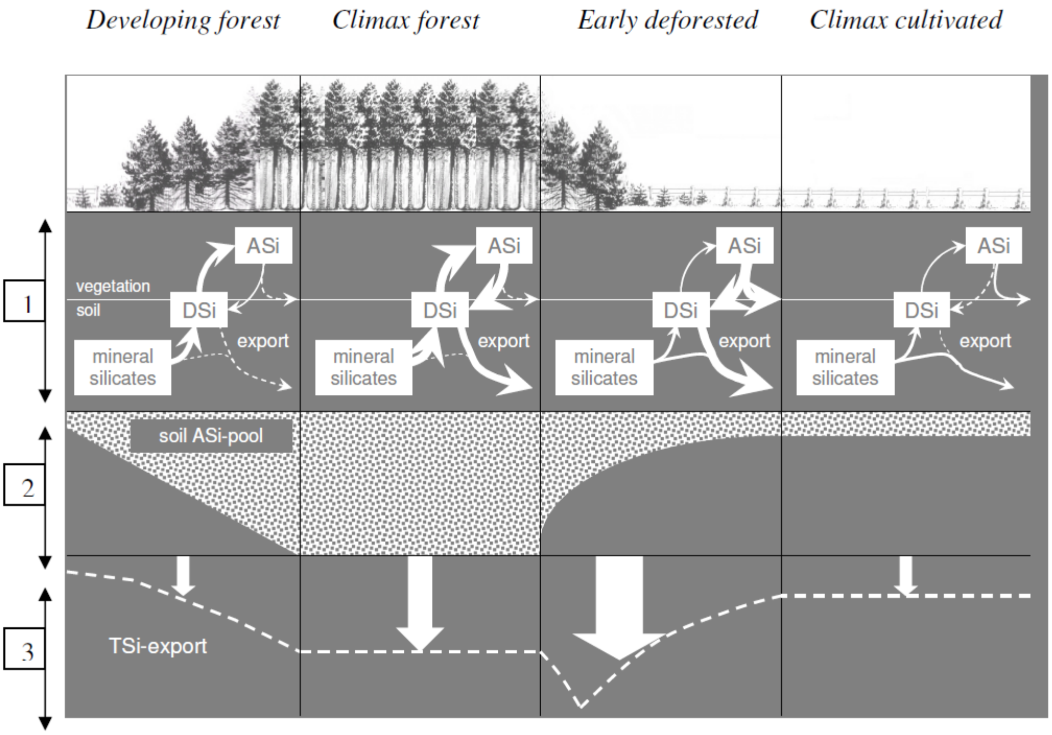
Our results and sustainable development

- Incorporation of our findings in models will improve their quality with respect to eutrophication in rivers and the coastal zone: the prediction capacity for eutrophication events will increase. As such, organizations such as OSPAR and the EU in general can benefit from our results. We will provide all data in ready-to-use datasets to MUMM (Management Unit of the North Sea Mathematical Models), for public archiving.

- 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. 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 BSi and DSi. Once implemented in biogeochemical models, our data will provide valuable input for the integrated management of watersheds.



Summary figure: A 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.

Keywords: biogenic silica; eutrophication; land use; deforestation; Scheldt river basin

2. Introduction and background

2.1 The geological Si cycle

The Earth's crust consists primarily of silicates (Si oxides, 90% of all minerals); consequently silicon is the second-most abundant element in the earth's crust (28.8%) after oxygen. During silicate weathering dissolved soil CO_2 is used in a reaction where Si is released from the crystalline structure of silicate minerals. In the environment dissolved silicate (DSi), ortho-silicic acid (H_4SiO_4), is transported through soil and exported to rivers and eventually the ocean. The silicate weathering process consumes CO_2. For example, in the weathering of anorthite to kaolinite, DSi is produced and CO_2 is consumed.

$$CaAl_2Si_2O_8 + 2.CO_2 + 8.H_2O \rightarrow Ca^{2+} + 2.Al(OH)_3 + 2.H_4SiO_4 + 2.HCO_3^-$$
$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2CO_3$$

The weathering of silicates is thus an important sink for atmospheric CO_2 on geological timescales (thousands to millions of years) and exerts a large influence on the global climate. Currently, global CO_2 consumption by chemical weathering is estimated to be ca. 0.26 Gt $C.yr^{-1}$. Ultimately, CO_2 is recycled back to the atmosphere by tectonic processes (metamorphic decarbonation and volcanic outgassing). The concentration of CO_2 influences the rate of silicate weathering; the weathering rates of silicates have changed significantly during the development of the biosphere (Struyf et al. 2010a and references within).

2.2 The biological Si-pump

DSi is an essential nutrient for the growth of diatoms (*Bacillariophyceae*). Diatoms take up DSi and use it to build their siliceous cell wall or "frustule". Consequently, transport of continental DSi to the oceans is an important component in oceanic primary production, a large part of which consists of diatoms. Forty percent of all oceanic C sequestration (~1.5-2.8 Gton C yr^{-1}) can be attributed to the growth and sedimentation of diatoms.

Although primary production through different groups of marine phytoplankton also results in a net CO_2 flux towards the sea bottom (the "biological carbon pump"), a crucial difference exists between diatoms and coccolithophores, an important sub-group of non-siliceous phytoplankton. Coccolithophores are characterized by calcite shells (=coccoliths); CO_2 is produced when calcium reacts with hydrogen carbonate during calcite formation (the "carbonate counter pump"). Therefore, an increased dominance of coccolithophores decreases the net sequestration of CO_2 and consequently the flux of CO_2 from the atmosphere towards the ocean floor. The biological carbon pump in the ocean is often referred to as the "biological Si pump" (Struyf et al. 2010a and references within).

Changes in Si inputs to marine ecosystems, especially in the coastal ocean, can significantly influence the species composition of oceanic primary producers, especially the balance of production between diatoms and non-siliceous phytoplankton. It has been hypothesized that a higher contribution of diatoms to total oceanic phytoplankton biomass occurred during the Last Glacial Maximum (79% vs. 54% today) as the result of increased eolian inputs of Si. This demonstrates that a link exists between Si transport from terrestrial to oceanic systems, atmospheric CO_2 concentrations and variations in global climate (Struyf et al. 2010a and references within).

2.3 Si and 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. 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. Essentially, eutrophication is triggered by excess input of the nutrients N and P into 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.

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). 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: understanding precisely the mechanisms contributing to eutrophication in the North Sea is a necessity for effective remediation.

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.

2.4 Ecosystems and the coastal-terrestrial link in the Si-cycle

Diatoms deplete oceanic and coastal DSi concentrations to a concentration near limitation for the production of new diatoms (<5 µM DSi). Most of the DSi sequestered by diatoms, e.g. 97% of the settling ASi, is recycled back to DSi before it is buried in ocean floor sediments. However, without continuous replenishment of the remaining 3% from terrestrial ecosystems, diatom production in the ocean would gradually decline on the long term, with important repercussions on carbon burial and oceanic production.

On geological time scales, the ultimate source of the continental Si flux to the oceans is the weathering of Si containing minerals.

Weathering rates result from the complex interaction between precipitation, runoff, lithology, temperature, topography and vegetation. Land plants and soil microbiota influence the weathering process of silicate minerals in different ways: through production of organic chelating ligands, through alteration of pH, through production of organic acids and CO_2, and through alteration of physical properties of the soil (e.g. physical weathering of rocks, increases in the surface area, longer residence time of water).

The link between the continental Si flux and characteristics of terrestrial ecosystems is receiving increased attention. In 2002, Conley published the first estimate of the size of the annual uptake of DSi by vegetation and its importance in terrestrial ecosystems. The global annual phytolith production was estimated to be 60-200 Tmole Si yr^{-1}. In comparison with the oceanic biogeochemical cycle, the global annual terrestrial BSi production is of the same order of magnitude as the global oceanic ASi production by diatoms (~240 Tmole yr^{-1}). By comparison, the annual release of Si by weathering of silicates has been estimated to be ~19-46 Tmole yr^{-1} and the terrestrial production is one order of magnitude larger than the global annual riverine input of DSi to the oceans (5 Tmole Si yr^{-1}). The amount of BSi buried in soils is several orders of magnitude larger than the annual terrestrial production. In addition, BSi transport from the continents by rivers constitutes a substantial part of Si fluxes into the ocean. The contribution of DSi release by phytoliths to the total DSi efflux from terrestrial ecosystems is observed to vary from about 10% to 30% in pine forests and forest tundra to almost 90% in forested Hawaiian stream basins (e.g. Derry et al. 2005). Important differences in Si cycling exist between different terrestrial ecosystem types and the highest amount of phytoliths are found in "soils" of coastal and inland swamps, flood plains, grasslands and forests. Plant species composition also influences soil Si content.

2.4.1 Forests

An intense biogeochemical cycling of Si is observed in forest ecosystems. Biotic fluxes through forests have been shown to be comparable to macronutrients such as Ca.

DSi concentrations in soil solutions of forested podzols are almost entirely biologically controlled. During summer, DSi released by weathering of minerals and dissolution of phytoliths is largely taken up and stored as BSi by forest vegetation. In winter and early spring, dissolution of phytoliths in the litter layer controls the DSi flux out of the forest system as mineral weathering is highly temperature dependent. Silicon uptake by forests was estimated to result in a 30% lower annual DSi flux out of a partly (60%) forested (oak and eastern white pine) watershed. The biogeochemical Si cycle was modelled in a temperate fir forest soil and an estimated average of 60% of the biogeochemical cycle of Si was controlled by biological processes (e.g. Gérard et al. 2008).

2.4.2 Grasslands

As most graminoid species are known as strong Si accumulators, grassland ecosystems store large quantities of BSi. Dissolution of DSi from phytoliths in different grassland ecosystems was shown to be several times larger than net weathering release by minerals and high BSi amounts in soil result in a significant buffering capacity of grasslands during periods of low stream DSi concentrations. Grass phytoliths are 10 to 15 times less soluble than forest phytoliths as a result of the latter's greater surface area (Blecker et al. 2006).

2.4.3 Wetlands

Wetlands are shown to accumulate large quantities of BSi. Freshwater and saltwater marshes in estuaries are important reservoirs of Si through burial of BSi and play an important buffering role for estuarine Si cycling. During summer, freshwater tidal marshes (Scheldt estuary, Belgium) were observed to contribute up to 50% or more of total DSi discharge. Inland wetlands have also been shown to be important regulators of riverine DSi transport. DSi concentrations were observed to be higher in stream basins with high wetland coverage in boreal watersheds (Struyf & Conley 2009).

2.5 Project goals

Although relatively few ecosystem studies have been made, all published studies point to an intense terrestrial biogeochemical cycling of Si. Therefore, terrestrial ecosystems cannot be neglected as active part of the biogeochemical cycle of Si and can be expected to play a major regulating role for the transport 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 lies the relevance 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) and for a correct understanding of links between Si and C cycling. 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.

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.

2.6 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, characterizing 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, BSi and DSi in at least 40 sub-basins with different ratios in land use types (agriculture, forest,…).

- to provide a first estimate of the spatio-temporal dynamics of human landscape interferences in ecosystem Si cycling, by integrating results obtained at several scales in a novel conceptual model for the Scheldt river basin

- to provide direction to future research on land use and silica cycling, suggesting and applying novel analytical techniques and by testing newly established concepts by looking into agricultural harvesting fluxes of Si and temporal variation in Si stores in ecosystems after human disturbance

3. Methodology

3.1 Overview

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.

- Sub-basin scale sampling campaigns map 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.

- In the second phase of the project, results from research at all scales were implemented in a new conceptual model and linked to other nutrient cycles

- To test the conceptual model, during the last phase of the project, focused and innovative research was performed on the parallel agricultural cycle of Si and on land use and Si fluxes in land use age gradients (in cooperation with Lund University, Sweden)

- During the second phase of the project, we also performed a methodological experiment, fine-tuning the used extraction procedures

- Based on our experiences, we summarized how future research should build on our results to advance research on bio-Si filtering in terrestrial ecosystems

3.2 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).

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

3.2.1 Rainfall simulations

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…).

3.2.2 Small catchment scale

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.

3.2.3 Subsurface mobilization of Si

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 BSi differs among plant species. Grasses (crops) are known to strongly accumulate Si (Conley 2002). The harvest of crops might remove large amounts of BSi 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.

3.3 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 a 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.

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

All sediment samples were analysed for BSi content using the sequential alkaline extraction procedure. BSi is extracted from the oven-dried sediment (25 mg) in a 0.1 M Na_2CO_3 solution at 80°C. Subsamples are taken after 150, 210 and 270 minutes. The extraction solution is then analysed for DSi concentration. BSi 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 BSi 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 BSi; despite its flaws, BSi wet-alkaline extraction is for the moment still the most representative method to analyse for BSi. All water samples and extraction solutions were be analysed for DSi content spectrophotometrically on an IRIS ICP (Inductively coupled Plasma Spectrophotometer).

3.5 Fine-tuning of methodology

The correct analysis of biogenic silica concentration in natural waters is crucial if one wants to correctly quantify terrestrial and/or riverine BSi fluxes. As the suspended particulate matter concentration (CSPM), and therefore σ, cannot be exactly known a priori this requires that the effect of solid-sloution ratio (σ) on measured BSi concentration (CBSi) is understood and that the effects of variations in σ can be accounted for. The objectives of this chapter are (i) to investigate whether and how variations in σ values affect measured CBSi in river runoff samples and (ii) to investigate whether or not it is possible to define a range of σ within which CBSi in runoff and/or soil samples can be accurately measured. For the laboratory experiment 30 runoff samples with a wide range of CSPM, typical for the Belgian Loam Belt, were prepared and analysed using the alkaline digestion method.

30 runoff samples with a wide range of CSPM were prepared by mixing a known amount of oven-dried (50°) soil, sieved at 2 mm, with a known quantity of distilled water. CSPM of artificial water-sediment mixtures varied between 0.1 and 100 kg m-3: this is

the range which is generally encountered in field situations. The soil used in the experiments was silty loamy subsoil sampled in central Belgium. Grain size analysis using laser diffraction showed that the soil had 7.8% clay (<0.002 mm), 79% silt (0.002-0.063 mm) and 13.2% sand (0.063-2 mm). Organic matter content was ~ 0.94% (n=5). The BSi content of the soil, as measured with the standard De Master method at a fixed σ value of 1.2 kg m^{-3} was 1.8±0.3 mg g^{-1} (or 0.18 ± 0.03 % wt, n=5).

In order to test for reproducibility, extraction procedures for 5 and 25ml filtration volume were conducted simultaneously by two different lab-entities in the Dept. of Biology of the University of Antwerp (A) and in the Dept. of Earth and Environmental Sciences of the Katholieke Universiteit Leuven (L). These four measurements series are referred to as A5, L5, A25 and L25. Afterwards, the relations retrieved were compared statistically by introducing a dummy variable which allows to test the hypothesis of coincidence, i.e. whether or not the regression relationships retrieved are significantly different.

3.6 The agricultural Si cycle

For the major crops (Table 1), representative samples were taken from selected agricultural fields throughout Flanders. Aboveground biomass was sampled directly before harvest.

Crop species	**Harvested part**	**Area (ha)**	**Yield (ton/ha)**	**Production (ton)**
Zea mays (fodder)	total biomass	114644	49,66	5693374
Beta vulgaris	Beet	25362	73,68	1868650
Solanum tuberosum sp	Potato	37928	46,12	1749332
Triticum aestivum	Grain	74390	8,81	655151
	Straw	74390	4,34	323045
Poaceae sp	total biomass	121210	6,56	795446
Zea mays (human consumption)	Grain	40238	11,99	48265
Hordeum vulgare	Grain	13657	7,60	103813
	Straw	13657	3,57	48733
Triticale x Triticale	Grain	4035	6,86	27695
	Straw	4035	4,04	16297
Linum usitatissimum	Grain	3578	6,30	22533
	Straw	3578	0,88	3154
Avena sativa	Grain	821	6,51	5344
	Straw	821	3,35	2750

Table 1: Overview of most relevant agricultural crop plants in Flanders (i.e. accounting for 96% of total agricultural production in 2008). The amount of cultivated area, yield and production numbers (all based on agricultural production numbers for 2008) is summarized. .

Source: Statistics Belgium, Belgian Ministry of Economy

3.7. Si cycling along land use age gradients

Silica pools within Swedish soil profiles were assessed for various land use types (pasture, agricultural land and forested landscapes) and at various landscape positions. The selected sites have similar soil properties, geological history and topography to make them geomorphological comparable, but differ in land cover history. Therefore two locations were selected in southern Sweden: Siggaboda and Råshult.

Siggaboda is an isolated nature reserve in southern Småland near the border with Skåne and Blekinge, Sweden (56° 27'N, 14° 12'E). The nature reserve (71 ha) has been continuous forest since 2700 years and is co-dominated by beech (*Fagus*) and pine (*Picea*). Signs of anthropogenic influences are lacking. Deglaciation took place 14500 years ago, the terrain is moraine with boulders covering a granite base.

Råshult is a culture reserve near Älmhult, southern Småland, Sweden (56°36'N, 14°11'E). The area has a typical infield-outfield structure with traditionally tilled crop fields and hay meadows in the vicinity of the farm and grazing areas, both pasture and forest, on a distance. Soils are typical of moraine material overlying a granitic gneiss bedrock with a moderate fertility. Both areas can be classified within the boreal-nemoral vegetation zone. They have a mean annual precipitation of 700mm y^{-1}. The mean annual temperature is about 5°C, with the July mean lying between 15-16°C, and the January mean lying between -2°C and -3°C.

The oldest indications of human influences are graves and cairns (piles of stones) date back to the Bronze Age 1000-500 BC. Reconstruction of basic land use conditions and human influences comes from information gathered with paleoecological techniques (e.g. pollen-analysis). The first permanent settlements in southern Sweden arose during the early Iron Age (500 BC-400 AD), while farmers abandoned the area in the late Iron Age. In 12 and 13th century people settled again in this area. First official records were made in 1545, and since then the area was continuously traditionally managed and subject to general changes in land reformation.

In fertility studies, the addition of Si in various forms to crops has been shown to have many beneficial effects.

Therefore, several procedures to determine the Si available for plants in soils have been developed. A distinction is made between water-soluble Si and solutions with a low ionic activity. The most common technique applies a $CaCl_2$ solution.

H_2O extraction

Various studies reported that soil fertility, as shown by crop yield, was significantly related to water-soluble Si content of soils. However a specific method to test Si water-solubility in soils is lacking. In hydrological studies water-soluble Si can be used to make estimations of Si concentrations in soil pore water and generation of Si leaching throughout the soil.

In this paper two different methods are applied to test their ability to determine water-soluble Si content. Both methods apply different water holding conditions: (a) unsaturated and (b) saturated conditions. For method A soil water samples were prepared by mixing ultra pure water (Milli-Q) with homogenized soil samples (0.1 kg) to field capacity. This standard method provides an appropriate mimic for field conditions because most soil water is held at or below field capacity and is then flushed by occasional rainfall events. With exception of short periods of saturated flow, nearly all water in soils is subject to unsaturated flow for long periods before leaching. After 48 h of equilibration the samples were centrifuged at 4000 rpm (Derry et al., 2005).

In method B complete saturation is applied. 3 grams of oven dried soil (<2mm) was shaken (horizontal movement) with 30ml ultra-pure (Milli-Q) water in a centrifuge tube for 4 hours. The suspension was centrifuged at 4000 rpm. For both methods the supernatant was filtered at 0.45µm (Chromafil® A-45/25) and analyzed for Si by the automated molybdate-blue method.

$CaCl_2$ extraction

The weakest extractant after water is CaCl2, which only extracts the easily soluble Si pool. 2 g of dried soil (< 2mm) is shaken (linear movement) for 16 hours with 20ml 0.01M CaCl2 extractant (1:10 ratio) in a 50ml Nalgene tube at 20 degrees.

After centrifuging at 4000rpm for 30 minutes, the supernatant is filtered at 0.45µm (Chromafil® A-45/25) and analyzed for Si by the automated molybdate-blue method.

4. Results and discussion

4.1 Fine-tuning the methodology

In Fig. 1, total extracted silica concentrations measured after 2.5 h of extraction time ($C_{TXSi_{2.5}}$) are plotted against σ. We found a poor relationship between C_{BSi} and σ for one series of measurements (A25) for $\sigma < 1.6$ kg m^{-3}. The A25 measurement series differs significantly from all other series indicating incoherence. Therefore we did not include this series in our further statistical analysis. However, implications and possible reasons for this incoherence will be discussed later in the paper.

Over the total range of σ three domains can be distinguished:

- Domain (1), $\sigma \leq 0.8$ kg m^{-3}: $C_{TXSi_{2.5}}$ increases linearly with σ: $C_{TXSi_{2.5}} = 76.3*\sigma$ (R^2=0.92, n=38),
- Domain (2), $0.8 < \sigma \leq 4$ kg m^{-3}: $C_{TXSi_{2.5}}$ increases degressively with σ and a power function can be fitted: $C_{TXSi_{2.5}} = 72.1*\sigma^{0.72}$ (R^2=0.91, n=32),
- Domain (3), $\sigma \geq 4$ kg m^{-3}: $C_{TXSi_{2.5}}$ remains constant: 225±44 µM (n=40).

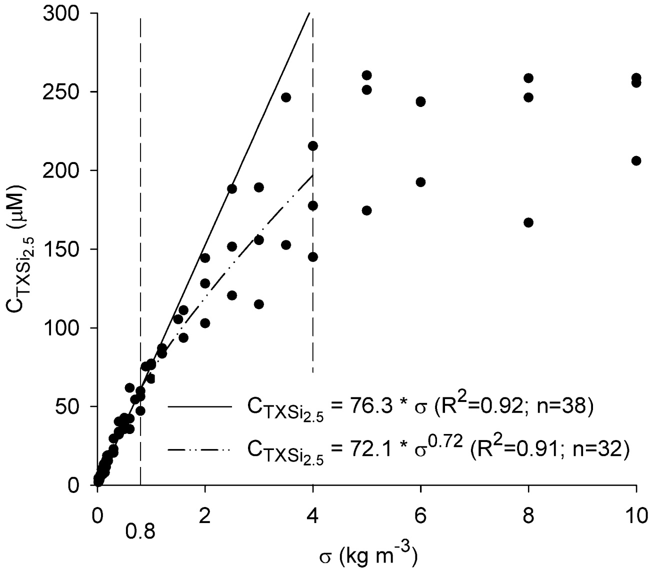


Fig. 1: $C_{TXSi_{2.5}}$ vs. σ; dashed lines indicate the limits between the different domains

When extraction slope (MDS) is plotted against σ, the same three domains can again be distinguished (Fig. 2): (1) a linear relationship for low σ values (≤ 0.8 kg m^{-3}): MDS = 0.0044*σ (R^2=0.89, n= 17), (2) a degressive increase for intermediate values of σ ($0.8 < \sigma \leq 4$ kg m^{-3}) where the relationship can be described through a power function: MDS = 0.0037*$\sigma^{0.61}$ (R^2=0.64, n=14) and (3) a highly variable MDS when σ exceeds 4 kg m^{-3} .

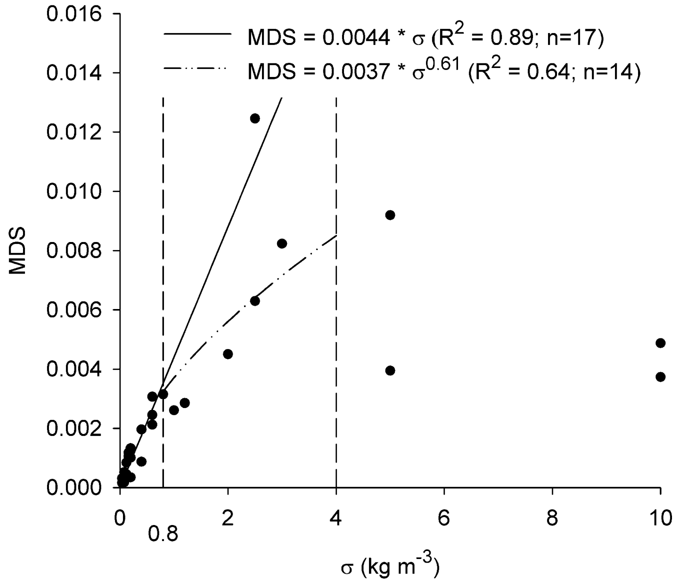


FiG. 2 MDS vs. σ; dashed lines indicate limits between domains for the vs. σ relationship

The analysis of our data reveals important limitations of the alkaline extraction procedure at high σ values. Complete dissolution of BSi should lead to a linear relationship over the whole range of σ values between $C_{TXSi_{2.5}}$ and MDS on the one hand and σ on the other hand. For our samples, these relationships were only linear when σ was below 0.8 kg m^{-3}. Above this threshold value, both $C_{TXSi_{2.5}}$ and MDS do no longer increase linearly with σ indicating incomplete dissolution. The fact that $C_{TXSi_{2.5}}$ does no longer increase linearly with σ is explained by the fact that the BSi present within the sample is no longer completely dissolved within 2.5 hours, when too much sediment is present. MDS is also expected to increase linearly with σ as mineral dissolution should be proportional to the amount of sediment (and therefore mineral silica) present in the sample. However, when σ exceeds a value of 0.8 kg m^{-3} the coupling is no longer linear, indicating that, similar to the dissolution of BSi, the dissolution of mineral Si becomes increasingly impeded with increasing sediment amounts.

The reduction of dissolution rates with increasing σ values may have two causes. First, Si dissolution is a surface process: as σ increases, it is no longer certain that all sediment surfaces are free and can contribute to the dissolution process. Second, saturation may occur with an increasing amount of sediment and dissolvable Si in the sample: the total potential extractable amount of silica with the 0.1M Na_2CO_3 alkaline extraction procedure is gradually reached. The absence of any clear relationship between σ on the one hand and $C_{TXSi_{2.5}}$ and MDS on the other hand once σ exceeds 4 kg m^{-3} is a clear indication that saturation is indeed reached. For the lowest σ values (< 0.1 kg m^{-3}) we observed a large variability in our results: this probably indicates that the accuracy limits of the method have been reached. Measurements errors with respect to the quantity of sediment on the filters become too large to allow for an accurate assessment of $C_{TXSi_{2.5}}$ and hence C_{BSi} concentrations.

Our results indicate that we underestimate (1) total extracted silica concentrations ($C_{TXSi_{2.5}}$, µM) and (2) mineral dissolution slopes (MDS) once a threshold σ value of 0.8 kg m^{-3} is exceeded. It is clear that an underestimation of $C_{TXSi_{2.5}}$ results in an underestimation of C_{BSi} while underestimating the MDS evokes an overestimation of C_{BSi}. Thus both errors compensate each other to a certain extent. Fig. 3 shows the empirical C_{ASi} vs. σ for $\sigma \leq 1.6$ kg m^{-3}. For all measurement series, except A25 there was a very good match between the empirical and the theoretical values predicted on the basis of observed linear relations in domain 1. The three other measurements series are coincident (Table 2) and an overall regression can be fitted: $C_{BSi} = 52*\sigma$ (R^2= 0.98, n=39). This is comparable with the theoretical curve $C_{BSi} = 52.8*\sigma$. We do not have a solid explanation as to why the results for the A25 series are different from those of the three other series. The fact that the measured values are consistently lower than the theoretically expected values may indicate that small variations in treatment (e.g. subsampling, filtration, shaking) result in noticeable discrepancies, which indicates the necessity of using a strongly standardized sample treatment procedure.

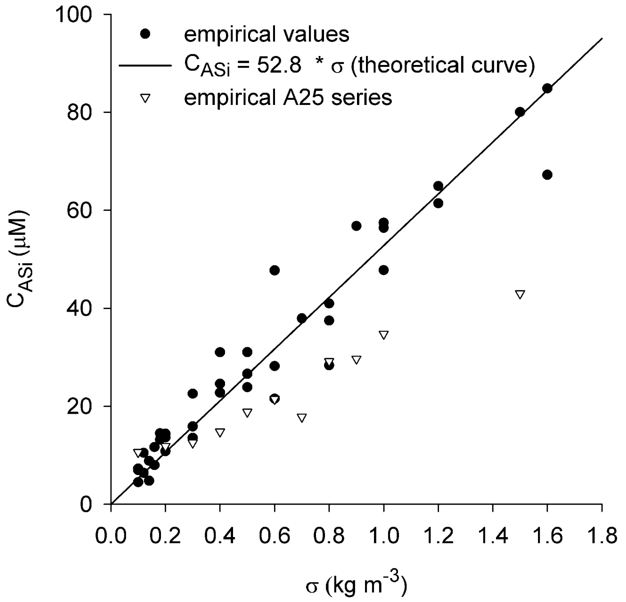


Fig. 3 C_{BSi} vs. σ within 0.1 < σ ≤1.6 kg m-3 for the empirical L5, A5 and L25 series.

Series	***Dummy***	***N***	***F-value***	***p-value***	***Sign. Difference***
L5 vs A5	L5= 0 & A5= 1	28	3.3	0.0528	No
L5 vs L25	L5= 0 & L25= 1	25	1.3	0.3025	No
L5 vs A25	L5= 0 & A25= 1	25	25.9	0.0001	Yes
A5 vs A25	A5= 0 & A25= 1	25	17.9	0.0001	Yes
A5 vs L25	A5= 0 & L25= 1	25	0.8	0.4791	No
A25 vs L25	A25= 0 & L25= 1	22	28.6	0.0001	Yes

Table 2: Dummy analysis for CBSi vs σ regressions at a significance level of 0.05 in the range 0.1 < σ ≤1.6 kg m^{-3}.

Our study confirmed that the alkaline (0.1M Na_2CO_3) digestion method can be used for runoff samples provided that the solid to solution ratio (σ) is within certain limits: at very low σ (<0.1 kg m^{-3}), subsample heterogeneity results in high variability of measured C_{BSi} while at higher σ values (> 0.8 kg m^{-3}) incomplete dissolution of BSi as well as the reduction of mineral dissolution rates results in underestimated C_{BSi}. As both errors compensate one another, the range of applicable σ-values can be extended above the theoretically correct limit (1.6 kg m^{-3}).

We found that C_{BSi} can be determined reliably within a considerable range of σ. While this finding confirms the results from some studies, it differs from observations made by other researchers who found that measured BSi concentrations continued to rise with decreasing σ. This may be due to the absence of a fine reactive mineral fraction in our samples.

The finding that reliable measurements can be made within a relatively wide range of σ values ($0.1 \leq \sigma \leq 1.6$ kg m^{-3}) is important as it is now possible to propose a method for the measurement of BSi in runoff samples and derive some recommendations for BSi analysis, making a distinction between samples with a low and high C_{SPM}.

(i) Samples with low C_{SPM} (≤ 1.6 kg m^{-3}): stir sample thoroughly take a subsample of 5 or 25 ml and use standard procedure (see materials and methods). Determine C_{SPM} afterwards and use this to determine σ.

(ii) Samples with high C_{SPM} (> 1.6 kg m^{-3}, water is no longer clear): stir sample thoroughly and take a substantial subsample (100-300 ml) and use adapted procedure.

4.2 Land use and habitat scale Si mobilization

4.2.1 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 3.

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

Table 3 Overview of rainfall experiments conducted during the LUSi-project (N=130). 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 ($p > 0.32$).

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. BSi-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 (1m²) 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 BSi-loss is equally important, so although there is no significant difference between SPM-BSi relations for crops, there will be a significant difference in BSi-loss for the various crop and tillage types according to the SPM-transport.

4.2.2 Catchment scale

In the arable catchments, DSi concentration varied between 50-400µM. Fluctuations in DSi concentrations followed fluctuations in discharge. BSi concentration varied between 0-500 µM. 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 silica concentrations. The relationship between suspended particle matter and BSi confirms the existence of an important coupling between sediment export and total silica transport in arable catchments. Relative importance of BSi 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. From our agricultural catchment data it is clear that BSi 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 BSi concentration in the beginning of events (Figure 5).

.

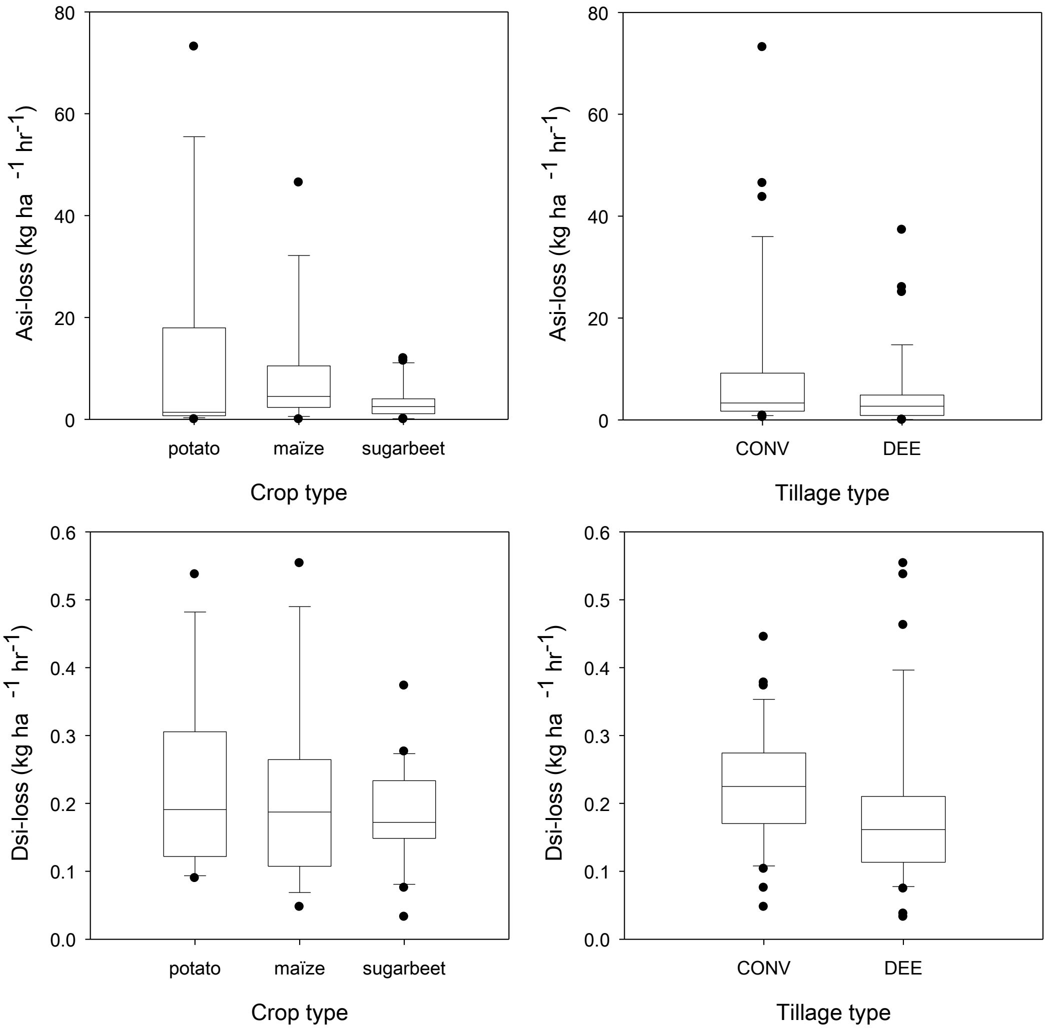


Figure 4: Boxplots for BSi (ASi in graph) (kg ha^{-1} hr^{-1}, top) and DSi losses (kg ha^{-1} hr^{-1}, bottom) during rainfall simulations for various crop type (left) and tillage type (right). Legend see Table 2.

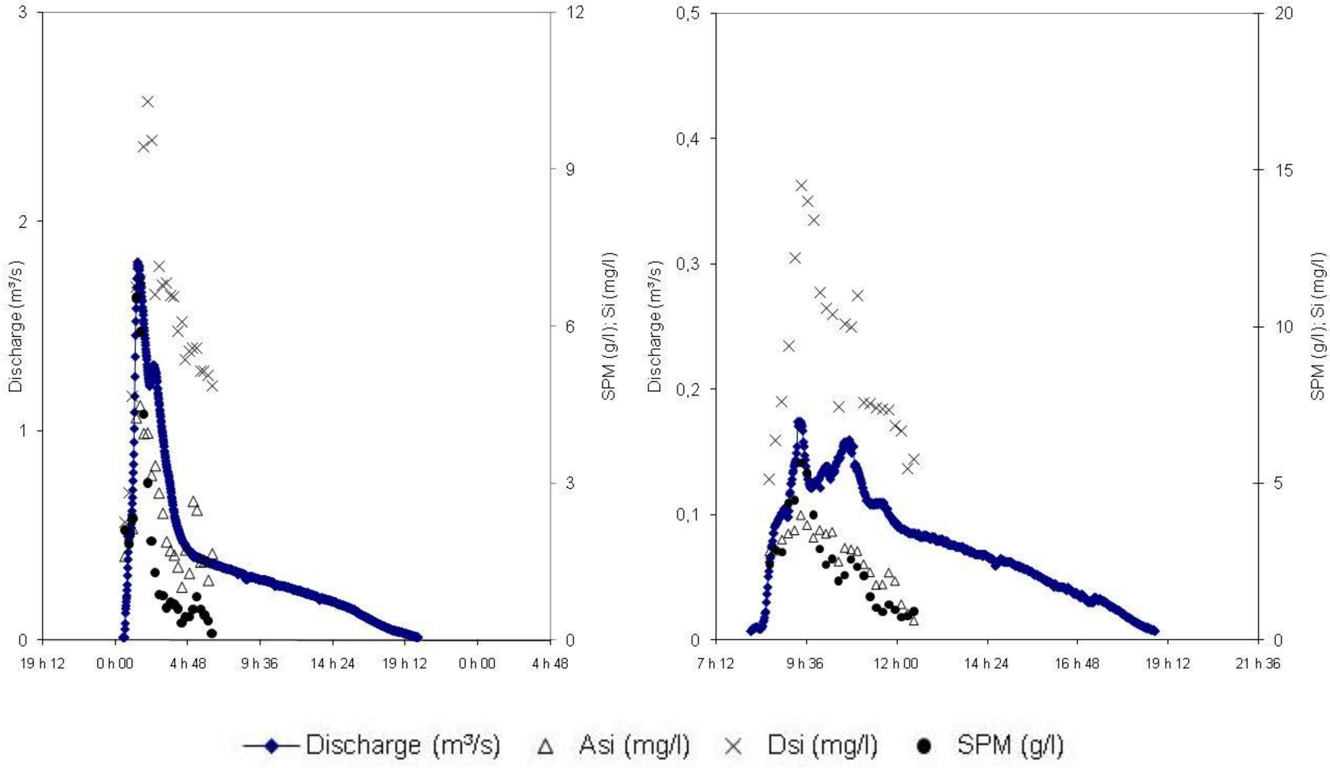


Figure 5: Example of 2 hydrographs at Velm: discharge (m³ s^{-1}), dissolved (cross) (DSi) and biogenic Si (ASi) and SPM.

For forests, 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 6). 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 BSi concentration mostly equal 0 but occasionally increase until 150 µM. During peak events BSi 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 BSi in peak-events maximum values are higher in the summer-autumn period then in the winter-spring period. For some winter-spring events BSi-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.

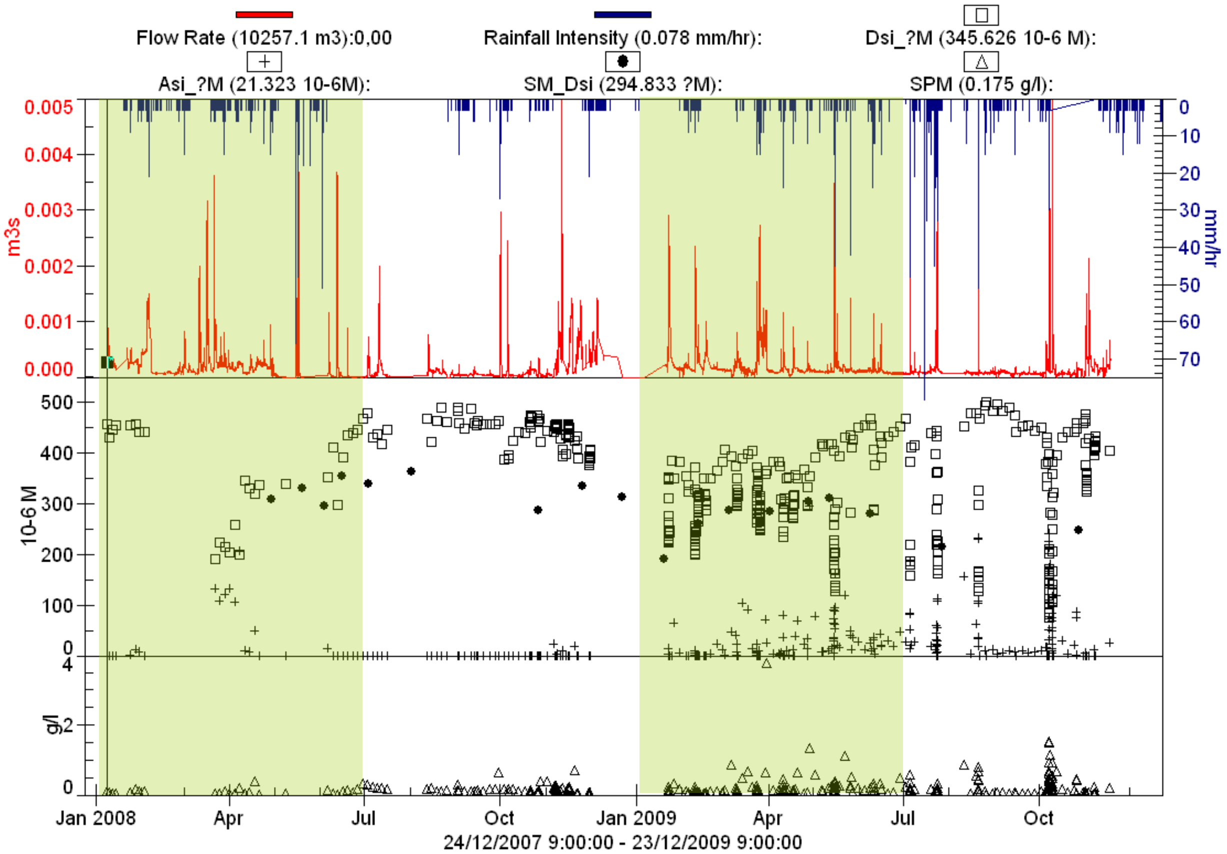


Figure 6 Overview of the Meerdaal data (‘08-‘09): discharge (red, $m^3 s^{-1}$), rainfall intensity (blue, mm hr^{-1}), dissolved (square) and biogenic silica (cross) concentrations (µM) for river samples, dissolved silica concentrations (solid circles, µM) suction cups and SPM (triangle, g l^{-1}) data.

For base-flow a median BSi concentration of 2µM and DSi concentration of 438µM result in an average TSi concentrations of 440µM with BSi 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 BSi transport. This is the case for both base-flow and peak-flow. Only severe peak-events will induce a significant BSi-flux. The most important hydrological pathways under forest are groundwater flow and subsurface quick through flow while overland flow is absent. Higher BSi flux during severe events result from gully bed disturbance. Peak-discharges evoke transport of fine particles and organic material and therefore BSi transport. This low attribution of biogenic 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 biogenic 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 7).

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.

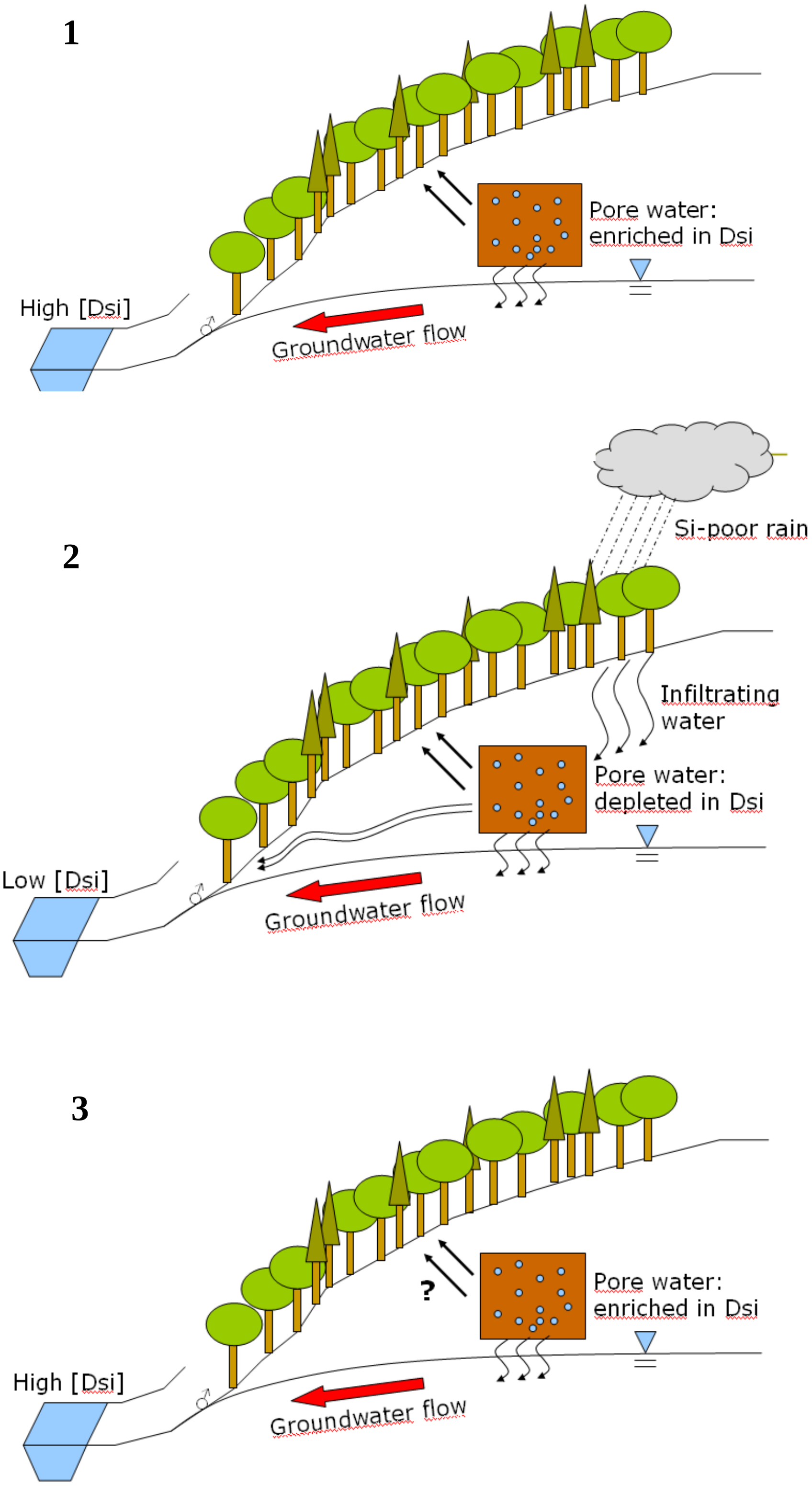


Figure 7: Dilution-flushing effect of DSi during peak-flow events in forested catchments

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

4.3.1 High-discharge events

In total, 432 DSi and 330 BSi 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 BSi concentrations increased with increasing discharge (Figure 8). SPM concentration showed a highly significant positive linear correlation with BSi concentration. Where analyzed, the relative amount of BSi increased significantly with the relative amount of organic matter (TOC) in transported SPM.

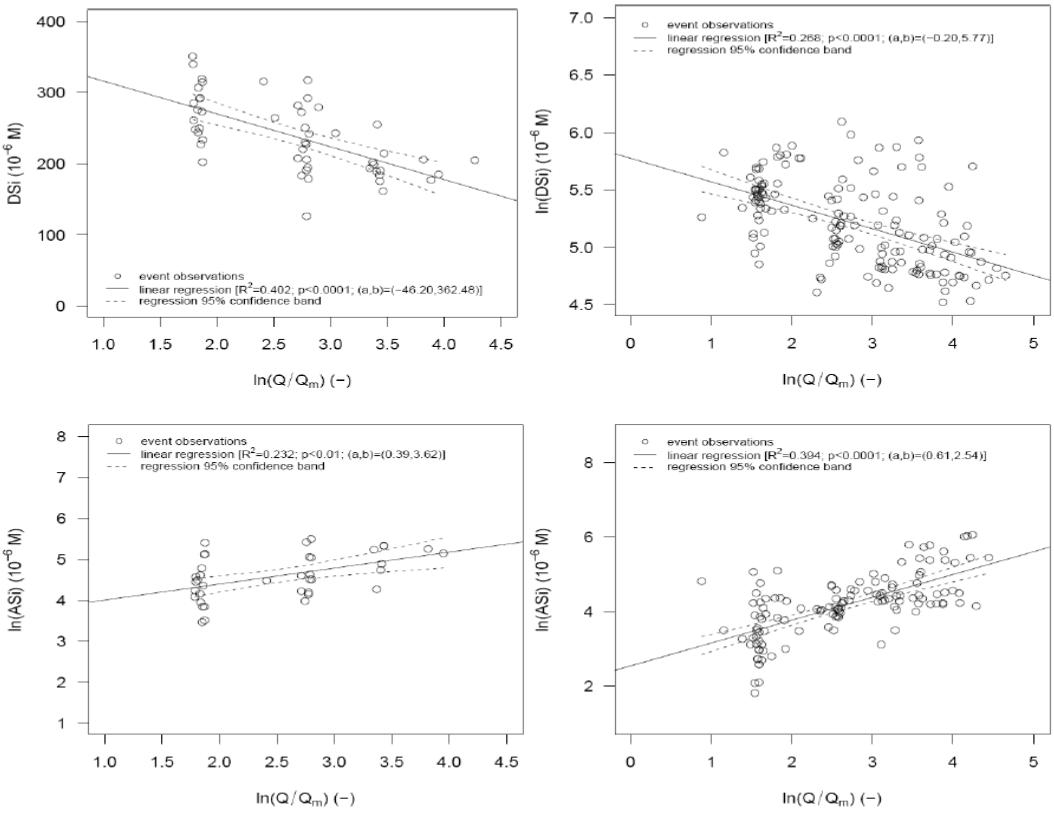


Figure 8: Relations between relative discharge (Q/Qmodal) and DSi - and ASi concentrations in the catchments of Leupegem (left) and Muizen (right). Qmodal is modal discharge from 2006-2008.

During peak flow events, the decreasing DSi concentration was largely compensated by (1) increases in discharge and (2) increases in BSi concentration. Consequently, DSi and BSi transport and the resulting net transported total bio-reactive Si (BSi + DSi) increased significantly during peak flow periods. The contribution of BSi 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 calculated that 6-40% of all bio-reactive Si was transported as BSi (Table 4). While around 35 to 45% of all water was transported during peak flow events, 68 to 75% of all BSi and 25 to 36% of all DSi was transported at the same time (Table 4).

		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

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. 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).

During peak events, a clear trade-off existed between DSi and BSi concentrations, and BSi 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 BSi concentrations in suspension both increase during the rising limb of the peak event. Yet, as explained above, the BSi content (% of transported material) of the mobilized sediment decreased exponentially when discharge increased. Still, as SPM concentrations generally increase with increasing discharge (BSi 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. These fluxes mostly result from the large-scale mobilization of sediments in the cultivated catchments. In such watersheds, it is clear that BSi dynamics should be included in silica transport budgets. Erosion physically mobilizes the BSi layers from the soil surface of the terrestrial ecosystems, and mobilizes them as suspended BSi into riverine systems. Recent research has emphasized the importance of these BSi 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 BSi from surface soil layers might hence also impact buffering of DSi transport through watersheds by ecosystem soils: the effect of this remains poorly studied.

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 BSi and DSi dynamics in the river continuum. While DSi is mainly associated with base-flow, BSi was almost completely transported during peak events. Increased intensity and occurrence frequency of events will result in increasing importance of BSi 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 BSi dynamics in upstream ecosystems, currently results in a poor quantification of BSi 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 BSi, explain the major differences (up to 200% and more) between modelled and observed Si fluxes at the catchment scale.

4.3.2 Base-flow

Fifty-one small watersheds were sampled in the Scheldt River basin for base-flow Si fluxes (Fig. 9).

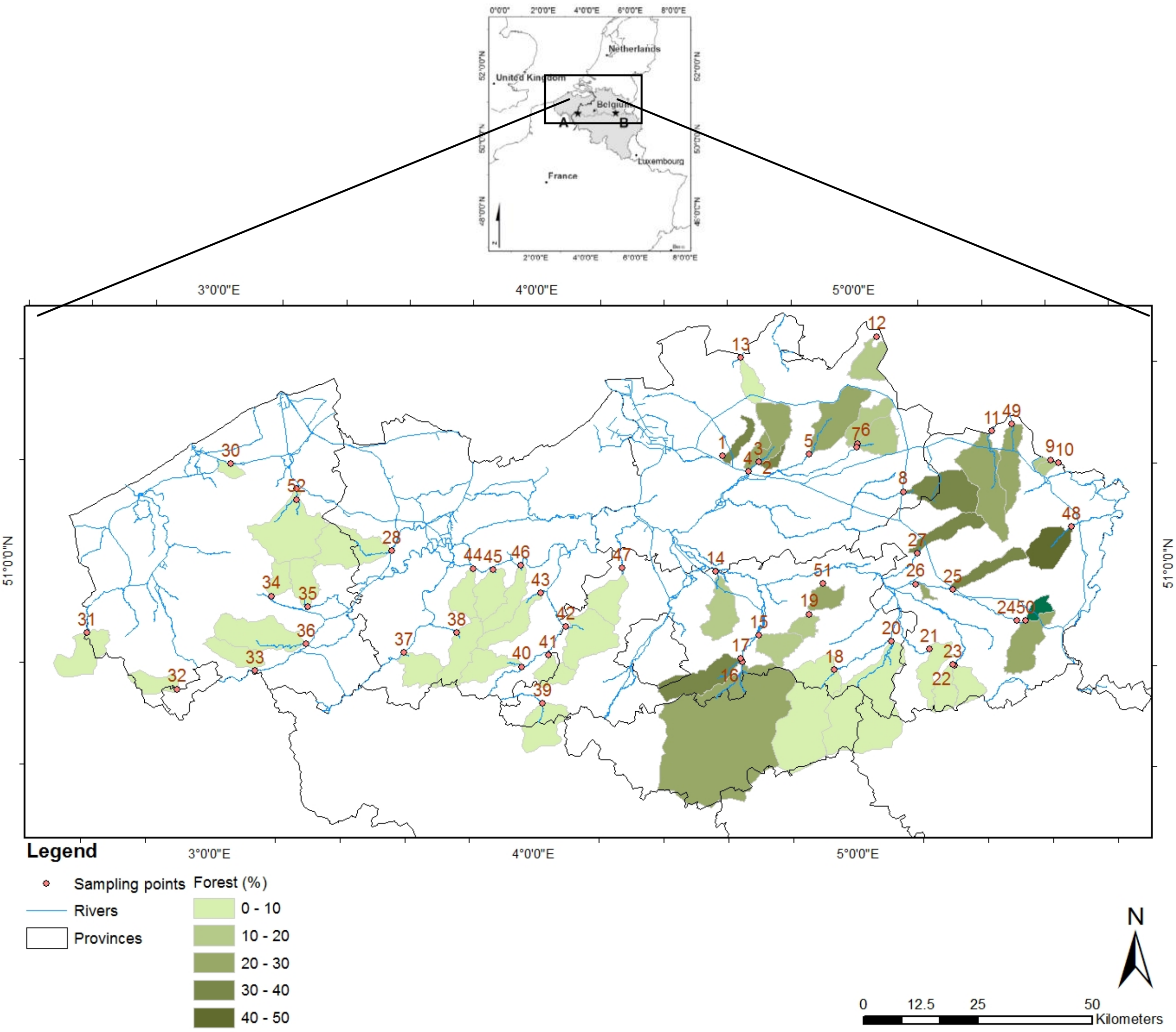


Figure 9: Location of catchments studied for sub-basin scale ASi and DSi fluxes and forestation degree.

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 (BSi + DSi) as the response variable, and three categories of explanatory variables (land use, soil texture and drainage class). Total biologically reactive silica fluxes (TSi, comprised of amorphous silica (BSi) 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 BSi 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 BSi 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). 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 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) 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. 10). 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.

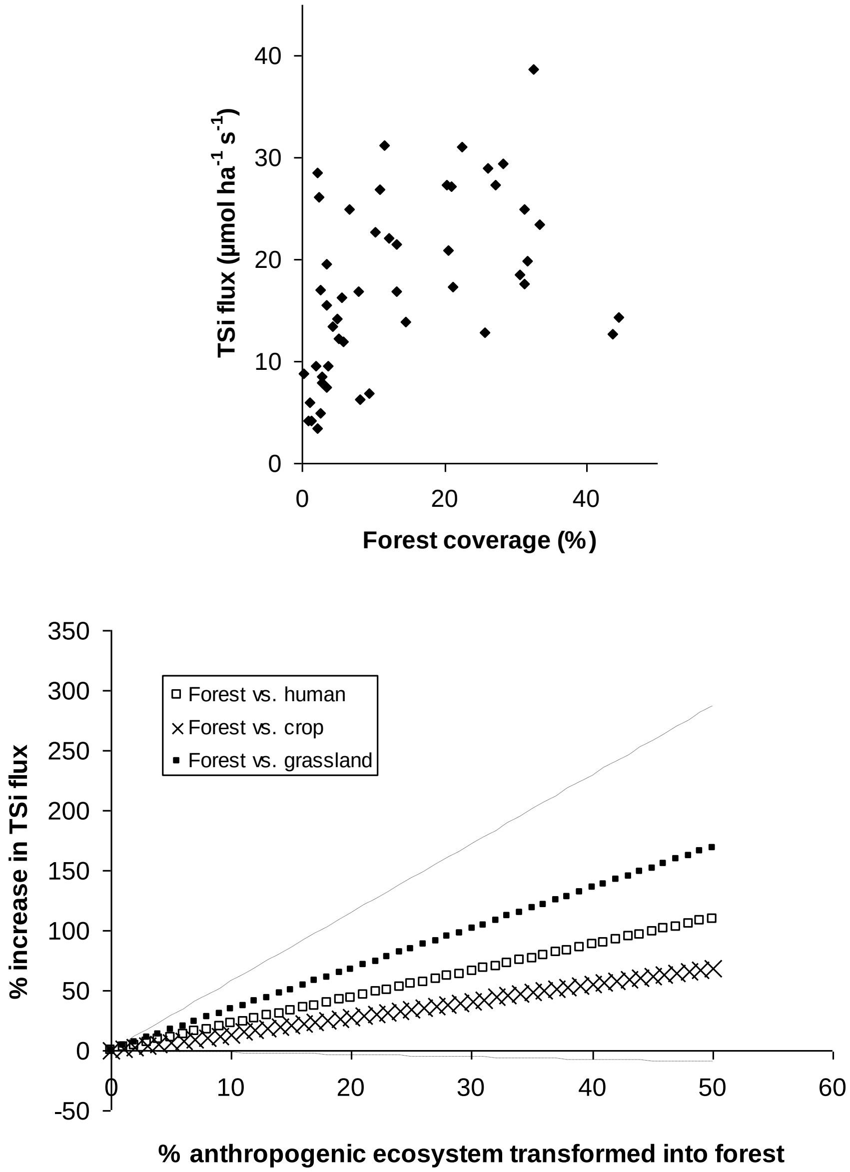


Figure 10: Deforestation and Si fluxes in the Scheldt watershed. Upper panel: variation of TSi flux (averaged per watershed) with forest cover. Lower panel: percentage increase in TSi flux coinciding with % increase in forest cover, as estimated from the mixed multiple linear regression analysis. The 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).

4.4 A novel conceptual model and its implications

Our 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. 11): 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 BSi pool, compared to the amount that is annually added to the vegetation and to the soil BSi 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 BSi stock (Cornelis et al. 2010).

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 BSi 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 BSi 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 BSi no longer balances the total amount of BSi dissolved, as harvesting of crops prevents replenishment of the soil BSi stock. Soil erosion will increase and BSi 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.

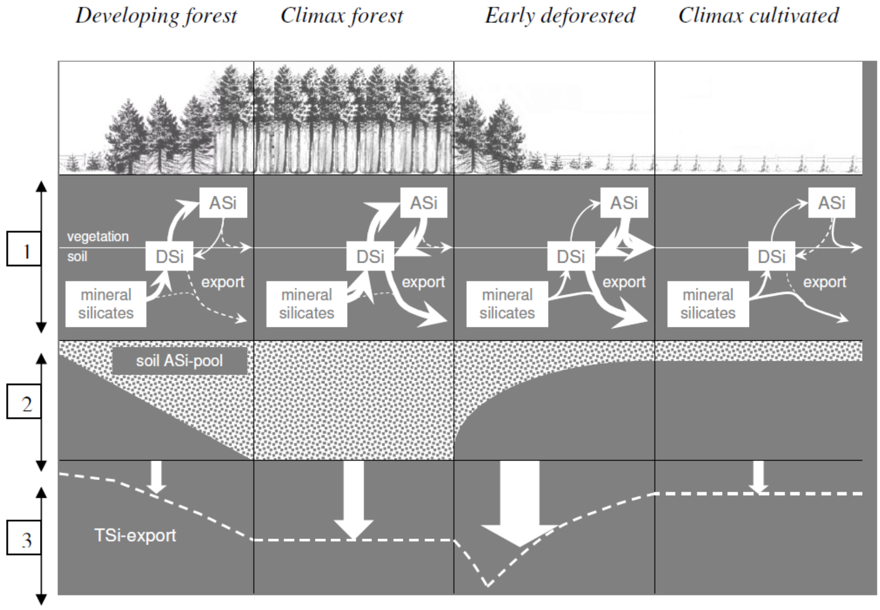


Figure 11: New conceptual model for changes in Si cycling with long-term soil disturbance. (1) Hypothesised Si cycling in developing forest, climax forest, early deforested areas and equilibrium cultured areas, the associated soil BSi (ASi in figure) stock (2) and the resultant magnitude of TSi export (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 BSi 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.

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 BSi stocks in the lower soil horizons will likely be incomplete: several mechanisms inhibit BSi 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 BSi through physical erosion, thereby further reducing the timeframe during which increased DSi export can be expected.

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 BSi has been depleted or immobilized. Grasslands and croplands behave similarly in our dataset. Grasses are known to accumulate significant amounts of BSi, resulting in the presence of a large phytolith pool in soils. 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 studies 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 BSi 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 BSi 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 BSi 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 ratios 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.

4.5 The parallel agricultural silicon cycle

Human land use potentially strongly interacts with continental mobilization of Si, yet research is still in a pioneer stage. A conceptual model about deforestation effects on Si-fluxes in a temperate European watershed was recently published (see 4.4). In the model, climax forest soils have stable or slowly growing soil BSi stocks. Export Si fluxes from these systems are mainly controlled by the dissolution of soil BSi (largely in the form of phytoliths) and consequent leakage of dissolved Si (DSi) from the system. Directly after deforestation, massive recycling of BSi leads to peak DSi fluxes, but sustained deforestation (> 500 years) eventually leads to an imbalance: soil BSi stocks become exhausted, and they are not replenished by new biomass due to crop removal. Absence of deep-rooting vegetation and soil organic layers prevents vegetation stimulated mineral weathering. This ultimately reduces Si export from deforested watersheds.

Worldwide conversion of natural ecosystems into agricultural land and consequent harvesting of crops introduces a new pathway in the biogeochemical Si cycle: the agricultural production Si cycle. Crop plants like rice (*Oryza sativa*), maize (*Zea mays*), wheat (*Triticum*), barley (*Hordeum vulgare*) and sugarcane (*Saccharum* sp.) all accumulate Si concentrations higher than 1% Si (of dry weight) (Ma et al. 2001). Cultivation and harvest of wheat or rice (annual export of 50-100 kg Si ha^{-1}) could deplete soil phytolith pools within decades, as estimated from an initial content of 1 ton $Siha^{-1}$ (Meunier et al. 2008). Global agricultural Si export has been roughly estimated at 210-240 x 10^{12} kg Si y^{-1} (Datnoff et al. 2001), which is in the same order of magnitude as total DSi transport by rivers to the ocean (0,14 x 10^{12} kg Si y^{-1}). Despite these indications of the importance of harvested crops for terrestrial Si budgets, no studies have currently aimed at quantifying it in more detail, and the fate of the biogenic Si in this large parallel cycle remains undiscussed. As a result, the agricultural Si cycle is not accounted for as a human influence on silica cycling at spatial scales from local to global. We performed a detailed quantification of the agricultural Si cycle in the Scheldt watershed (Flanders, Belgium), where the role of land use in silica fluxes was recently highlighted.

4.5.1 High BSi export fluxes

Highest production numbers were reached for total maize plants, beets and potatoes, followed by wheat and commercial grasses (Table 1), together accounting for 94 % of total agricultural production. However in terms of BSi concentrations ([BSi]), other plant species play a more dominant role. Cereals (esp. wheat straw) and grasses show highest [BSi], whereas potatoes, beets and maize grain accumulate almost no BSi (Table 5).

Generally, the same patterns can be seen in literature yet our crop samples show mostly lower [BSi] than literature values (Datnoff et al. 2001). Total agricultural BSi fluxes were between 23577 and 41000 ton Si a^{-1}. Harvest of maize and wheat only are responsible for more than half of this yearly export flux. When adding the mowing of commercially grass species, three quarters of yearly total BSi fluxes are accounted for. On average, between 46 and 70 kg BSi ha^{-1} a^{-1} is removed from the soil. Areas harvested for maize (fodder) in total accout for highest BSi fluxes, followed by harvest of wheat, mowing of grasses and removal of *Triticale* crops (Table 5). Despite high production values for potato and beets (i.e. together responsible for 30% of total agricultural production numbers, (Table 1)), these crops are of limited importance for agricultural Si export fluxes as they accumulate almost no BSi in their tissues.

Crop species (replica's)	**Harvested part**	**BSi concentration (mg/g)**		**BSi (ton y^{-1})**		**BSi (kg a^{-1} ha^{-1})**
		mean BSi	**min-max**	**mean BSi**	**min-max**	**total biomass**
Zea mais (3)	total biomass	2,42	2,26 - 2,56	13777,97	12867,96 - 14575,04	112,23 - 127,13
Triticum aestivum (6)	grain	7,76	3,31 - 8,37	5083,97	2168,55 - 5483,61	36,81 - 112,75
	straw	19,92	11,11 - 39,39	6435,06	3589,03 - 12724,74	
Poaceae (6)	total biomass	6,42	4,84 – 8,10	5106,76	3849,96 - 6443,11	31,76 - 53,16
Triticale x Triticale (3)	grain	6,73	5,51 – 7,63	186,39	152,6 - 211,31	35,84 - 44,15
	straw	8,95	8,49 – 9,33	145,86	138,36 - 152,05	
Avena sativa (6)	grain	3,65	2,92 – 4,76	19,51	15,6 - 25,44	19,48 - 26 52
	straw	6,67	5,89 – 7,20	18,34	16,2 - 19,8	
Hordeum vulgare (3)	grain	2,47	1,68 – 3,10	256,42	174,41 - 321,82	14,5 - 24,22
	straw	6,07	4,79 – 7,06	295,81	233,43 - 344,05	
Zea mais (3)	grain	0,38	0,34 - 0,42	183,41	164,1 - 202,71	4,08 - 5,04
Solanum tuberosum (3)	potato	0,11	0,07 – 0,16	192,43	122,45 - 279,89	3,23 - 7,38
Beta vulgaris (3)	beet	0,07	0,04 – 0,11	130,81	74,75 - 205,55	2,95 - 8,1
Linum usitatissimum (3)	grain	0,45	0,43 – 0,51	10,14	9,69 - 11,49	0,71 - 0,86
	straw	0,42	0,38 – 0,47	1,32	1,2 - 1,48	
Total flux					**(*) 23577 - 41002**	**(°) 46,3 - 70,3**

Table 5: Overview of crop species sampled in the Flemish Scheldt basin. For different plant parts, [BSi] and agricultural BSi fluxes are summarized. *Poaceae* sp. consist mainly of *Vicia* sp., *Holcus lanatus* and *Arrhenaterium elatus*. Fluxes were calculated based on production and surface data for 2008. Estimations for total fluxes are indicated in bold: (*) lower and upper limit of total agricultural BSi flux in 2008 and (°) lower and upper limit of BSi flux per unit of area, weighted over the area of cultivated land for different crop species.

Results indicate that total agricultural BSi-export in our study area is situated between 23000 and 41000 tons y^{-1}, which equals the yearly TSi flux from the Scheldt towards the North Sea (i.e. ≈ 29000 tons; Struyf et al. 2004). As our study area only occupies 42 % of the Scheldt river basin and comparable agricultural development exists in the other parts of the watershed (respectively 56% and 61% agriculture in Flanders and in whole watershed), it can be easily assumed that at the watershed scale, agricultural Si fluxes double those we observed.

4.5.2 The forest-cropland opposition

Opposite to agricultural systems, climax forests are accumulating Si in the soil; Si uptake varies between 2 and 45 kg Si ha^{-1} a^{-1} and generally exceeds export Si fluxes (deciduous forest: 5-7 kg Si ha^{-1} y^{-1}; coniferous forest: 1- 10 kg Si ha^{-1} y^{-1}; Cornelis et al. 2010).

Forests are thus large reservoirs of reactive BSi, continuously processing Si between its initial release from mineral weathering, and its eventual export to rivers. Grasslands play a similar role: export fluxes of DSi from (semi)natural steppe and prairie grasslands can range from 0,2 to 11 kg Si kg Si ha^{-1} y^{-1} (Blecker et al. 2006).

Human intervention changes this equilibrium. Increased Si export was seen after deforestation (excess of 16 kg Si ha^{-1} y^{-1}), due to rapid dissolution of BSi pools in topsoil (Conley et al. 2008). However, when soil BSi pools are depleted, deforested watersheds (<5% forests, 10 kg Si ha^{-1} y^{-1}) show on average lower Si export fluxes compared to forested watersheds (>40% forestation, 30 kg Si ha^{-1} y^{-1}) (see 4.4). Sustained deforestation depletes the BSi pools, resulting in overall lower TSi export fluxes. A similar situation will be reached in grasslands managed for hay sequestration.

BSi amounts ending up in the agricultural loop are large compared to natural fluxes (e.g. >100 kg BSi ha^{-1} y^{-1} for wheat and maize). This should not surprise too much: agricultural fields are fundamentally different from natural ecosystems as they are managed to optimize harvest. In contrast to nitrogen and phosphorus, where uptake will mainly be supported by fertilizers, Si will mostly originate from natural sources. The Si uptake in vegetation, without replenishment of the soil Si pool, will eventually almost completely diminish soil Si pools, as has been observed in rice paddies, which are artificially fertilized with Si.

4.5.3 A big sink for Si?

The fate of BSi after it entered the agricultural production cycle is still an enigma. One could think that transfer of harvested Si to aquatic systems is only delayed, as it will eventually end up in sewers, wastewater and rivers anyway. There are however strong indications that this is not the case. Point sources of silica to the Seine river basin only constitute 8% of total Si inputs (≈ 2 kg ha^{-1} a^{-1}); with most coming from detergents (Sferratore et al. 2008).

Although little research has focused on the fate of harvested BSi, we hypothesize below that there are several major permanent BSi sinks.

Here we try to provide a first conceptual life cycle assessment (the entire life cycle of a product from raw material acquisition to final product disposal) for the harvested BSi (Fig. 12).

Part of the harvested crops will re-enter the cropland as green manure. This will only delay the depletion of soil silica pools, as biomass is never fully reapplied. A major part of the crop BSi is consumed, either directly (e.g. fodder, cereals) or indirectly, as raw material for final products (e.g. bread and beer). In fluids, Si is present as orthosilicic acid and readily absorbable in the gastrointestinal tract. The bioavailability of phytolithic silica in food has been suggested to be lower (Van Dyck et al. 1999), yet other studies showed similar absorption values in foods as for fluids (Jugdaohsingh et al. 2002). Human and animal bodies (bone and connective tissue) therefore constitute potential sinks for Si. Animal bones can end up in industrial applications such as gelatin, which is commonly used as a gelling agent in food, pharmaceuticals, photography, and cosmetic manufacturing.

Human feces will eventually end up in the sewers. The effect of different wastewater treatment techniques on the Si concentration in effluent water remains unstudied so far. While suspended BSi becomes concentrated in the sludge and is eventually removed, some of the effluent might actually be enriched with DSi, as DSi dissolves into the influent after coming in contact with the accumulating organic matter. Enrichment might especially occur in grass-based wastewater treatment systems, as the plant litter in these is potentially strongly enriched in BSi.

The sludge from wastewater treatment systems will be treated by incineration and/or landfill. As it can be contaminated with other waste products (e.g. heavy metals), it is usually stored isolated from river water or re-used in industrial applications. Sludge treatment techniques are subject to rapid development (e.g. Wang et al. 2008): tracking the fate of Si after wastewater treatment (both in sludge and in effluent water) could shed completely new light on Si pathways after human harvest.

Animal manure can be restored to croplands, yet government programs regulating manure application have also led to treatment of concentrated livestock wastewater in artificial wetlands (sinks for BSi; Struyf and Conley 2009) or the use of manure in e.g. the production of biofuel. Biofuel and ash remaining after fuel combustion forms another big Si sink. Sugarcane and cereal grains are primary constituents of first generation biofuel, while complete crops and straw are now used as input for second-generation bio-fuels (e.g. Gressel 2008). Though land application of bio-solids remaining after waste water treatment or biofuel combustion receives increasing attention, its current application is, for both technical and legal reasons, limited (e.g. Wang et al. 2008).

To complicate matters, manure, crops and food are traded and transferred across the globe in massive amounts. Some countries are net exporters, some are net importers, implying that worldwide transfer of manure might enrich soils with biogenic Si in one place of the world, at the same time depleting BSi stocks in another part. As it is our current hypothesis that most of the harvested BSi is not re-entering river systems, on a single river basin scale it is unimportant whether the BSi is exported or not. However, if application of bio-solids from sludge on croplands would become more common practice, food transfers worldwide could have a similar effect as manure transfers.

4.5.4 Implications

The agricultural export of Si from croplands and grasslands is massive, potentially strongly interfering with biological control mechanisms on terrestrial Si mobilization. Besides the sinks discussed in the paragraphs above, there are several other potential options for commercial or industrial exploitation of crop biomass and associated BSi: traditional building materials, detergents, bio-plastics, textile, paper pulp … etc. Our results imply that a detailed life cycle assessment is necessary for harvested crop BSi, as it constitutes an enormous flow of BSi out of terrestrial ecosystems, currently unrecognized in biogeochemical Si cycling, depleting BSi stocks in natural environments which play a crucial role in the Si biogeochemical cycle.

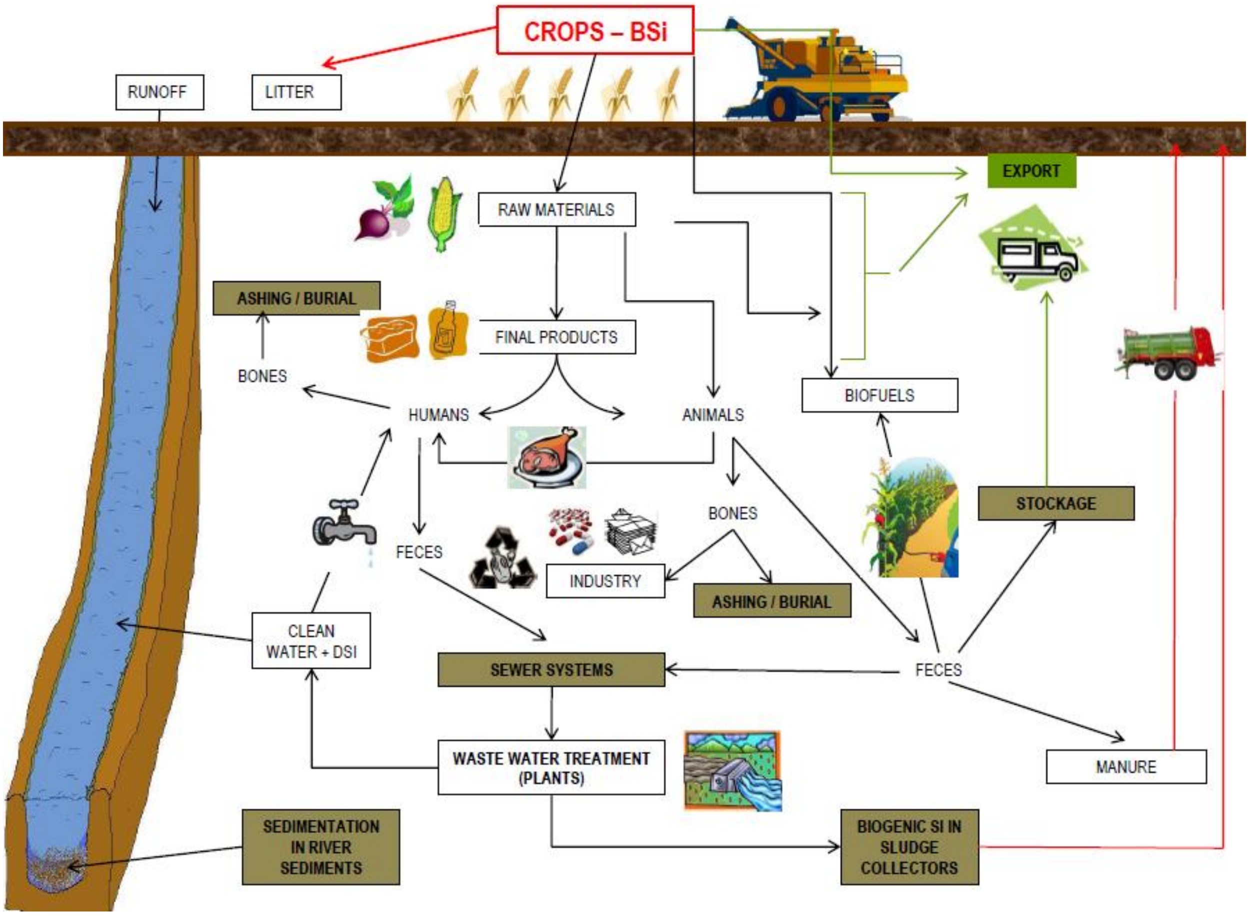


Figure 12: Preliminary life cycle assessment scheme ("Cradle to Grave") of harvested BSi for a typical agricultural watershed. Grey boxes represent potential sinks for biogenic Si. Red arrows indicate BSi fluxes being re-applied, as crops stay on the land, either directly (litter), as indirectly (animal manure). Green box and arrows indicate export related fluxes of crops and related materials out of the watershed.

4.6 Si pools and fluxes in land use age gradients

Sweden

Under all land uses the maxima of BSi are reached in the top layer, followed by a general downward trend of progressive decrease of BSi. There are some slight variations in distribution between land use types. Arable fields (Fig. 13) have a BSi rich top layer of only 0.05m. Under pristine forest the BSi rich top layer extends until 0.15m. Although BSi generally progressively decreases, under arable land BSi remains high until a depth of 0.25m before decreasing. This depth corresponds with typical plough depths of traditional tillage. Further 75% of the profiles under grassland, 50% under grazed forest, and all under pristine forest show a peak in BSi at intermediate depths (0.3-0.6m). This trend is obscured by averaging BSi for grazed forest and slightly recognizable for grassland.

In the top layers the distribution of Si_{CaCl2} is rather distinct from the BSi. Maxima in Si_{CaCl2} are reached at depth. Generally there is an increase with depth until it peaks between 0.25-0.6m and thereafter Si_{CaCl2} decreases again. A secondary trend for most grassland, grazed forest and pristine forest profiles is a dip between 0.1-0.25m in Si_{CaCl2}. So Si_{CaCl2} distributions in grassland, grazed forest and pristine forest show similar development as BSi, except the opposite trend in the top 0.25-0.3m. Si_{CaCl2} increase towards a maximum while BSi is accumulated in the top layer and afterwards decreases. Si_{CaCl2} are generally lowest for profiles under arable < grassland ≤ grazed forest << pristine forest (Fig. 14).

Belgium loam belt

BSi are constant over the top soil meter with an average around 2 g Si kg^{-1} for all different land uses, without any specific soil development (Fig. 15). Under grassland and forest there is enrichment in the top layer and a small increase at 0.7m. On average BSi are slightly higher under arable and grassland then forest.

In contrast, Si_{water} under arable land are one order of magnitude lower then both grassland and forest (Figure 16). Further there are also differences in distribution between both countries. Si_{water} decreases progressively under arable land in Sweden while Si_{water} are constant in Belgian. Grassland and forest soils have a similar development in both countries. A small dip at shallow depth afterwards Si_{water} increase towards a maximum; an extreme peak at 0.3m under grassland and a peak at 0.8m under forest.

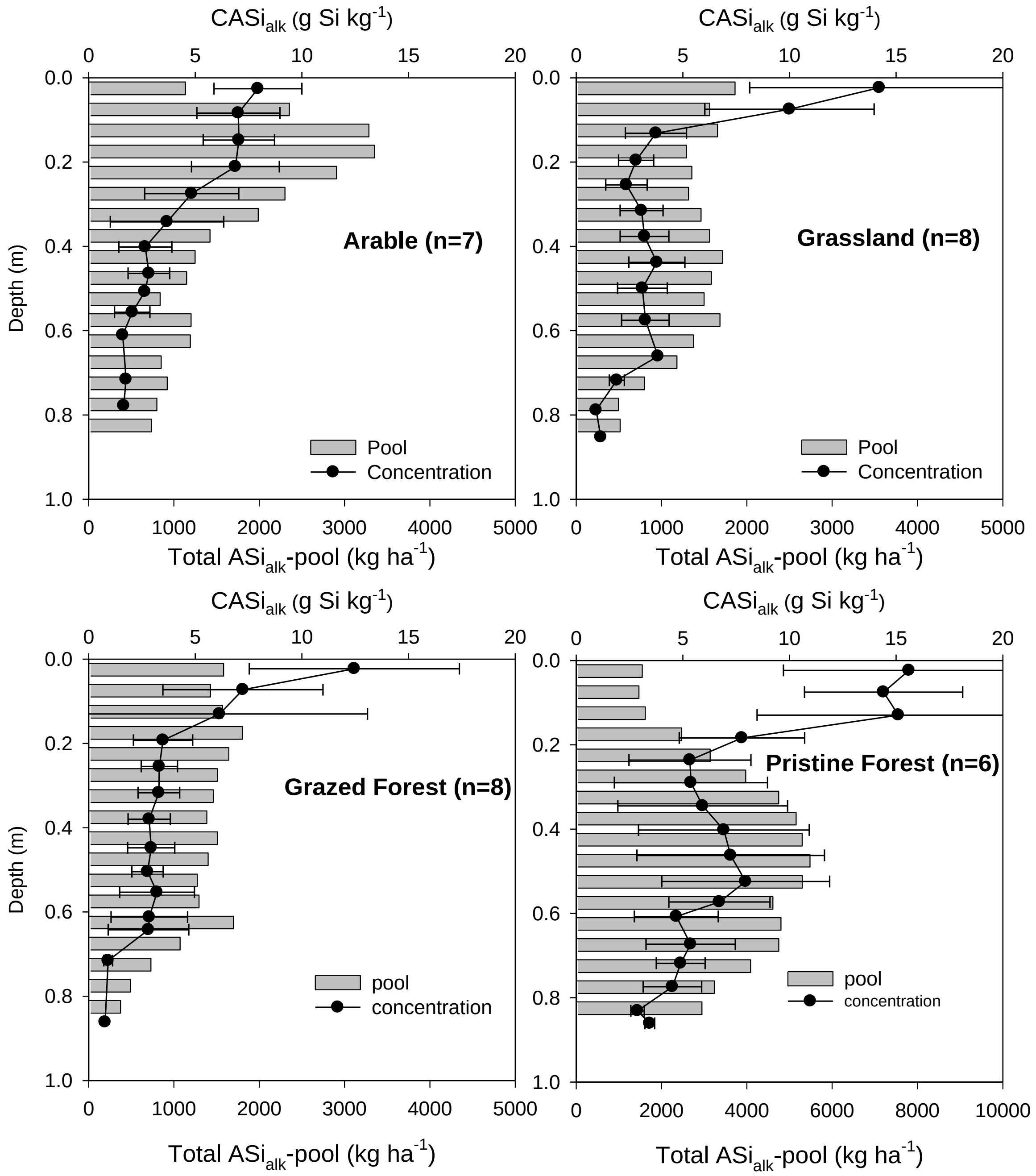


Fig. 13 Average distribution of alkaline (Na2CO3) extracted silica (CASialk, g Si kg-1 dry soil) and total ASialk-pools in soils under various land uses in Southern Sweden. N= number of profiles analysed under specific land use.

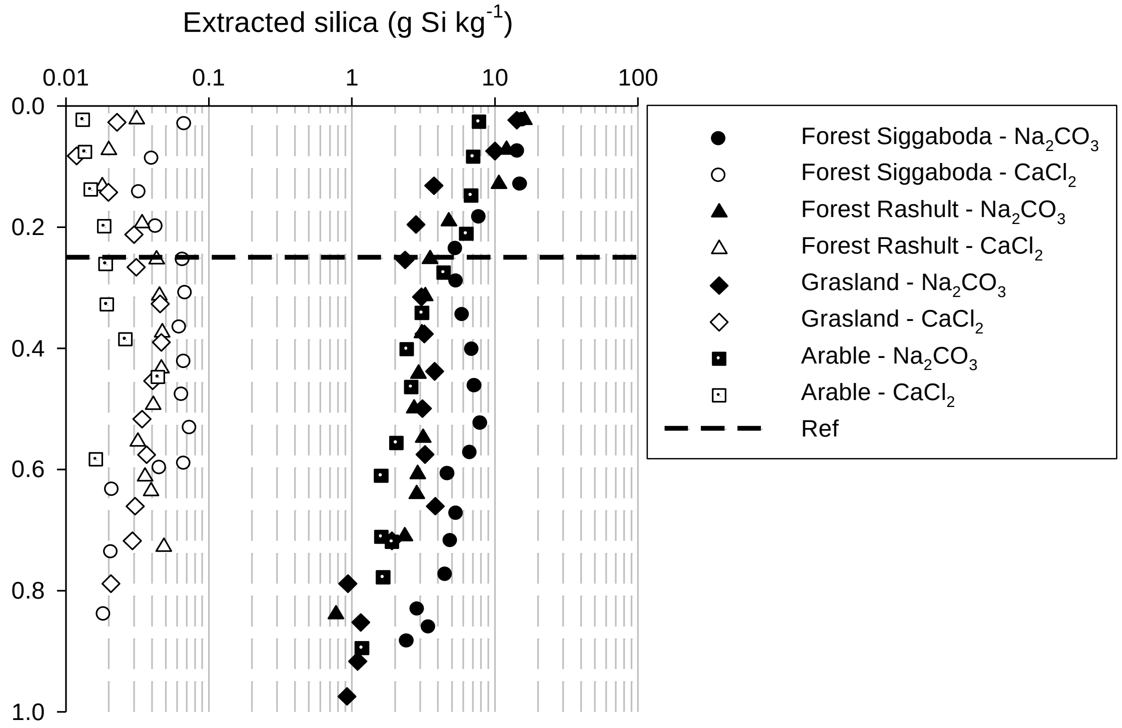


Fig. 14 Average distribution of alkaline extracted silica (Na2CO3) and easily dissolvable silica (CaCl2) in g Si kg-1 dry soil in soils under various land uses in Southern Sweden.

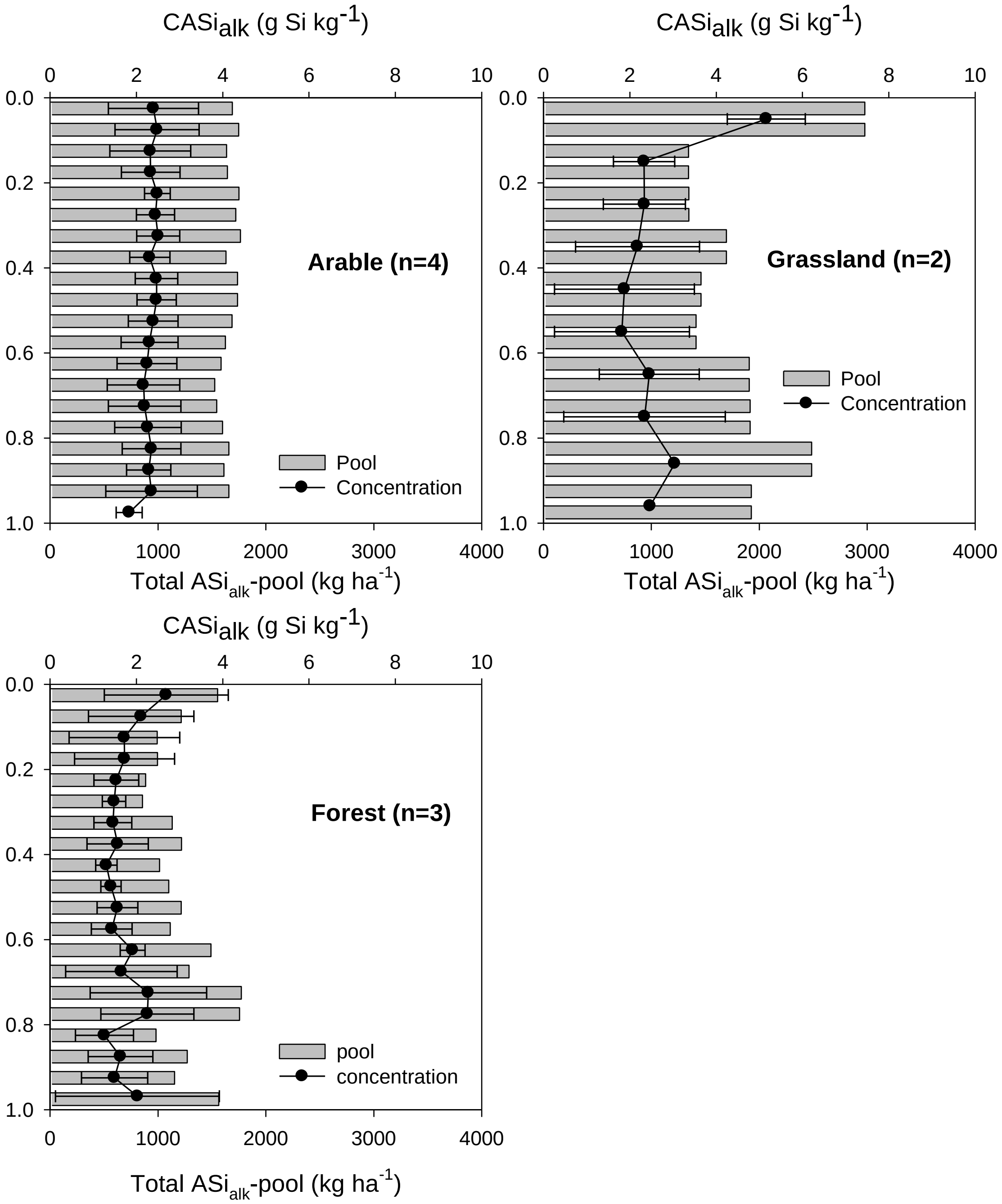


Figure 15 Average distribution of alkaline (Na2CO3) extracted silica (CASialk, g Si kg-1 dry soil) and total ASialk-pools in soils under various land uses in the Belgian Loam Belt. N= number of profiles analysed under specific land use

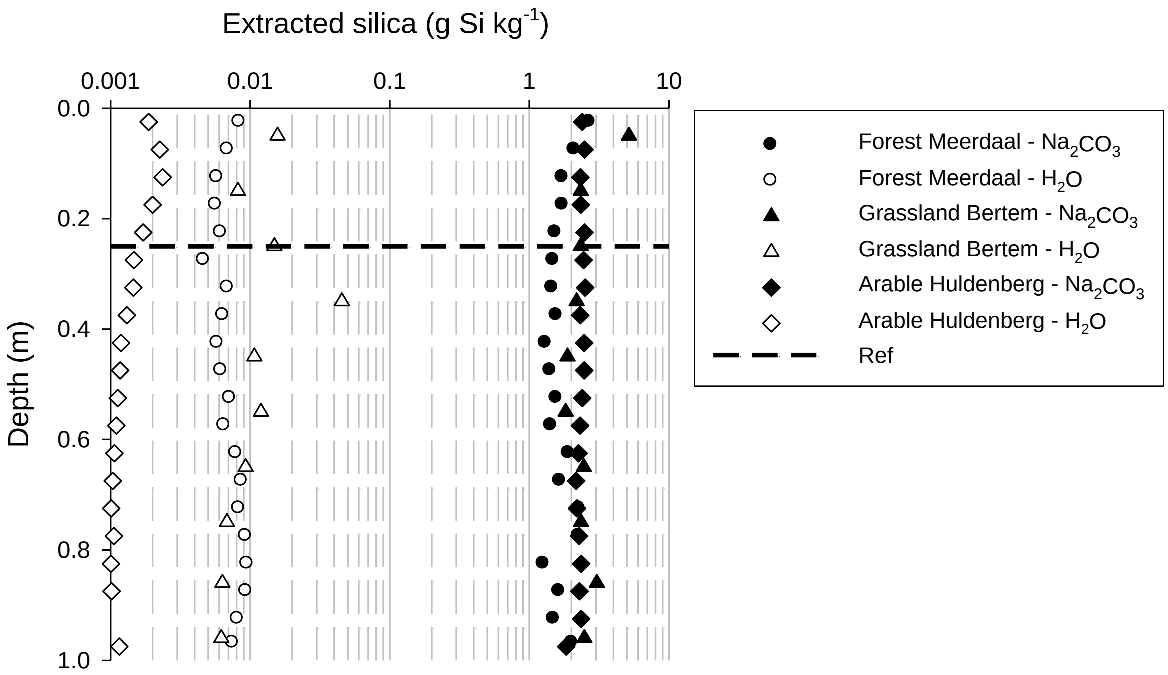


Figure 16 Average distribution of alkaline extracted silica (Na2CO3) and easily dissolvable silica (H2O) in g Si kg-1 dry soil in soils under various land uses in Southern Sweden.

Our conceptual model can be tested with these data. Siggaboda is our reference for the climax vegetation. The other investigated land uses in Råshult (grazed forest, pasture and arable land) have all experienced human impacts to varying degrees, and should be situated somewhere between the early deforestation and climax agricultural stages. The significant difference between BSi stock in Siggaboda and Råshult corroborate the conceptual model, indicating both sites are in a different stage with varying Si cycling. One could expect that agricultural land has significantly lower total BSi pools as it has been subject to the most intensive human impacts but there are no significant differences in total BSi pool between the three land uses.

The vertical distribution of soil nutrients is generally determined by leaching and biological cycling (Sommer et al., 2006). Leaching moves nutrients downward, and increases nutrient concentrations at depth. Biological cycling has the opposite effect. Nutrients are transported upwards through uptake and transport by vegetation, and recycled to the soil surface by litterfall and throughfall. Biological cycling creates a decreasing profile until root depth.

The accumulation in the top layer and occurrence of a peak at depth (0.25-0.6m) in BSi indicates the influence of both leaching and biological cycling on the Si distribution in Southern Sweden. The pristine equilibrium profile is the result of interaction between both processes. The large BSi pool in the top layer consists mainly of phytoliths and is determined by biogenic processes (Blecker et al., 2006), while at depth pedogenic processes are responsible for the increase in BSi defined as the translocation-accumulation of stable phytoliths, Si adsorption onto Fe oxides and the formation of pedogenic opal (. A similar translocation-accumulation process can create an accumulated Si rich horizon at depth that corresponds with the typical belly shaped distribution of Sialk pools in our pristine situation. The belly shaped feature is absent under arable land and remnant under grassland and grazed forest. The absence of a BSi pool at depth for arable land supports our conceptual model of Struyf. The transition towards arable land limits biological cycling to the top 0.3m, i.e. root depth.

Furthermore in Råshult traditional tillage is applied without heavy machinery. Plant remains are left in situ but these are insufficient to replenish the soil BSi stock. The balance between biogenic BSi input and BSi dissolution has been perturbed, resulting in a net loss. During the last five centuries the original deep pool became subject to increased dissolution, which resulted in a progressive decrease in BSi pool with depth. Although harvest limits biogenic input, BSi in the top 0.25m are comparable with both grazed forest and grassland. This can be explained by several processes (1) mulch and cover crop mixture during ploughing can act as an additional important biogenic BSi source and (2) ploughing and shallow root system enhance weathering of alumino-silicates by creating more reactive surfaces. Low organic carbon contents in the top layer support the second process. Furthermore the larger easily dissolvable (SiCaCl2) pools under grazed forest and grassland imply that arable fields have undergone a larger mobilisation of the labile BSi pool. A comparison of individual profiles showed that the belly features are more pronounced and common in grassland then grazed forest. Grassland had higher possibility to regenerate vegetation and more efficiently recycle Si then grazed forest. The difference in potential biogenic ASi delivery will influence the mobilization processes and also accumulation, and therefore differences in belly structure.

Both grasslands and grazed forest can be situated at a early deforestation stage in the conceptual model. Human impacts are significant but will not lead to a complete elimination of the BSi pool. Instead, a new equilibrium between biological cycling and leaching will develop. It is unclear if such a new equilibrium stage has been reached for grazed forest and grassland. Although total BSi pools are equal for all three land uses, the lower importance of the biogenic input to the BSi pool under arable suggests that arable fields have not yet reached a new equilibrium and are still under deterioration.

We can conclude that human activities influence BSi storage in Southern Swedish soils. The conceptual model has been corroborated. The transition of pristine forest towards grazed forest, grassland or arable land confirms the decline of the BSi pool and an important vertical redistribution after deforestation. Furthermore the transition has been more intensive under arable then grassland or grazed forest. Lower biogenic ASi input coincides with a higher mobilization in arable land, and an increased deviation from the original pristine equilibrium profile.

The differences between the Belgian and Swedish soils confirm that long-term deforestation completely diminishes the easily dissolvable Si pools; this provides explanation for the decreased Si fluxes we observed after long-term deforestation. The progressive decrease in easily dissolvable Si from pristine forest to long-term deteriorated arable land is in concordance with the conceptual model.

4.7 Emerging understanding of biological Si cycling in terrestrial ecosystems

Although a number of synthesis activities within the last decade have discussed biological transformations in the terrestrial silica cycle (Street-Perrott & Barker 2008; Struyf & Conley 2009; Struyf et al. 2010), the timescales associated with BSi storage and recycling in soils, the persistence and reactivity of BSi throughout the soil profile, the dependence of storage on ecological processes, the feedbacks to hydrology, the interaction with man's activities and ultimately the global relevance of BSi storage and recycling in silica budgets are poorly constrained.

Here we aim to identify the major gaps in our understanding of biogeochemical Si processing in terrestrial ecosystems. Through identification of key controls in the biogeochemical Si cycle, we hope to inspire research focusing on the intricate interactions between ecological, biological, chemical and physical processes controlling the global silica cycle. The impact of ecosystems on weathering intensity of silicate minerals, the role of ecosystems as filters in continental Si transport and the relative magnitude of the biologically controlled Si cycle compared to basic weathering should be a focus of future research efforts. We feel this can be achieved by addressing 5 key controls on ecosystem BSi cycling: ecosystem biodiversity, BSi dissolution rates and reactivity, hydrology, weatherability of silicates and anthropogenic impacts. This is not purely an academic question. The silica cycle is closely connected to the carbon cycle (Street-Perrott & Barker 2008). Mineral weathering of silicates is an important sink for atmospheric CO2: incomplete knowledge of the ecosystem Si filter impedes the accurate quantification of this sink. Moreover, the import of Si into coastal zones from the terrestrial environment is essential to sustain diatom growth. Diatoms play a key role in the oceanic C-sink and eutrophication of coastal zones.

Nutrient cycling in soils is controlled by four key processes: external nutrient input, nutrient export, internal nutrient translocation and nutrient transformations (e.g. Sommer et al. 2006). Mineral weathering of primary and secondary silicates constitutes the prime external source of DSi to ecosystems (Fig. 17). Plant uptake translocates DSi to BSi and is a key factor determining the uptake into the ecosystem Si reservoir. Other important biogenic pools are diatoms, sponges and testate amoebae (Aoki et al. 2007). We will discuss key factors that current research indicates are the main controllers of the processes occurring within the ecosystem BSi reservoir: these are the factors that will ultimately determine its importance in global silica cycling. We have not incorporated climate as a specific key factor: we feel that its impact will mostly be indirect through the key factors we identified. This doesn't mean that climate is not important: it is maybe the most important factor of all. It will impact on hydrology, on ecosystem diversity, on dissolution rates (through pH and temperature) and silicate mineral weathering. Understanding the effect of climate on the ecosystem silica buffer will therefore require a thorough and synergetic understanding of the effect of the key factors we identified.

4.7.1 Ecosystem biodiversity

We hypothesize that the magnitude and the size of the ecosystem Si reservoir will be strongly dependent on the occurrence of organisms specialized in the biological processing of Si. This may sound obvious, but surprisingly few studies have actually focused on biological Si storage and cycling at the ecosystem scale. Strong variability exists in plant biomass Si concentrations (Hodson et al. 2005). BSi concentrations in aboveground biomass can impact directly the BSi storage in ecosystem soils (e.g. Struyf et al. 2009). Other silica accumulating organisms also impact soil BSi content, especially sponges and diatoms in wetlands and in wet soils (Struyf & Conley 2009) and testate amoebae in forest soils and wetlands (Aoki et al. 2007). Increased diatom abundance during periods characterized by a transition in vegetation in Northern peatlands led to pronounced storage peaks of BSi in soil profiles (Kokfelt et al. 2009). Recent research has also indicated the capacity of wetland and aquatic macrophyte communities to store BSi (Struyf et al. 2005; Schoelynck et al. 2010).

Ecosystem Si storage can directly impact watershed scale Bi fluxes. A rare case study was described for an African mountain lake: development of high biomass vegetation dominated by grasses led to decreased DSi fluxes from the surrounding catchment into the lake, while nutrient poor vegetation in the catchments led to higher input of DSi into the lake (Street-Perrott et al. 2008). A similar observation was made in a Northern Sweden peatland-lake continuum (Kokfelt et al. 2010).

Quantitative mass-balance studies are necessary to improve our estimates of BSi storage and cycling within terrestrial ecosystems. However, the focus should now also shift to the impact of ecological processes on local BSi storage. We hypothesize that research focusing on connections between ecosystem biodiversity and the ecosystem BSi reservoir could well reveal that species' effects can be more important than abiotic factors (e.g. weathering, climate) in controlling ecosystem BSi storage, as was previously observed for other nutrients. We hypothesize that the increased storage of BSi in soils will favour dominance of Si accumulating plants. BSi concentrations in aboveground biomass can impact directly on BSi storage in ecosystem soils (e.g. Struyf et al. 2009).

Accumulation of BSi in soils will increase DSi availability in soil water (Struyf et al. 2009), due to the high solubility of BSi. Si-accumulators' ability to concentrate BSi in soils effectively engineers the accumulators' environment and increases their potential fitness, by creating a soil solution rich in a key nutrient. Uptake of Si by grasses and other accumulators positively impacts their competitive strength, and provides protection against several stress factors such as pollution, drought and physical damage (Epstein 2009). Wetlands are a good example: wetlands are rich in grasses and sedges and their occurrence is positively linked to BSi storage and DSi availability in soils (Struyf et al. 2009). A similar mechanism could be true for grass tussocks: tussocks potentially alter Si availability for grasses by recycling of BSi to DSi even before reaching the soil profile (like for other nutrients). Grasses are well-known to exert a strong influence on cycling and storage of other nutrients in soils, with impact greater than expected based on their biomass contribution to communities (McLaren & Turkington 2010).

Another link between ecosystem engineering and silica accumulation in plants has recently been shown for the aquatic species *Nuphar lutea* (spatterdock) (Schoelynck et al., unpublished). In this species, the underwater leaves create a low-dynamic environment ideal for the effective floating of the surficial photosynthesizing leaves. BSi storage in the underwater shoots and leaves is highest, when water current is highest. Silica is thus directly stored to increase resistance to physical damage and to create a suitable living environment. This raises questions whether other ecological adaptations might also alter Si storage in ecosystems. Studies focusing on ecological adaptations and BSi storage, will surely lead to the discovery of BSi storage gradients which are currently unaccounted for.

Patterns in BSi storage can also have a significant impact on ecosystem functioning. Grasses are well-known to employ silica-based defences against herbivores (Massey et al. 2007). Recent work in Kielder Forest in northern England indicates that silica defences in grasses play a key role in field vole (*Microtus agrestis*) populations (Massey et al. 2008). Grass-feeding mammals such as voles show dramatic population cycles which population ecologists have tried to understand for decades.

Massey et al. (2008) now show that declining vole populations were associated with high silica content in the grass species *Deschampsia caespitose* (tufted hair-grass), their winter food plant, while increasing vole populations occurred when silica content in the grass was low. This is a dramatic example of how silica content in vegetation serves as an ecological adaptation, and how changing environmental pressures may thus strongly alter Si uptake in the ecosystem BSi reservoir.

4.7.2 Dissolution rate and reactivity

Knowledge regarding the variability of BSi reactivity through soil profiles and across ecosystems is key to understanding the functioning of the ecosystem BSi reservoir, and should receive immediate attention from biogeochemists. Numerous BSi dissolution studies have been conducted for coastal, estuarine and oceanic diatom BSi, particulate matter and sediments, highlighting the importance of ambient DSi-concentrations and of external factors (pH, salinity) on BSi reactivity. Despite all these processes affecting dissolution and preservation rates of BSi, BSi reactivity in terrestrial samples remains literally unstudied. This is partly attributable to the fact that terrestrial BSi storage is currently studied using simple alkaline extraction methods or estimated from phytolith extraction, providing little insight in its composition and reactivity. Yet, as in the coastal environment, one expects a strong effect of ambient variables (temperature, pH) on the dissolution of terrestrial BSi. Studies combining quantification of BSi dissolution rates and its microscopic identification will potentially link key control one, ecosystem biodiversity, to key control two, reactivity.

We hypothesize that large reactivity gradients for BSi exist across ecosystems, but also within ecosystems. BSi is deposited by a diverse collection of organisms including diatoms, sponges, testate amoebae and plants (as phytoliths). Experimental studies have shown that structural changes to the BSi can affect the dissolution rate, and this directly affects its recycling and preservation in earth surface environments (Loucaides et al. 2010). Aluminum substitution into the surface matrix of BSi increases its preservation efficiency (Van Cappellen et al. 2002) and is an important mechanism for preservation of BSi in marine sediments. There is also a range of lithogenic amorphous materials in soils ranging from allophanes, imogolites to clay minerals that differ greatly in their structure and reactivity (Sommer et al.

2006). These can interfere with extraction procedures. It is indeed important to realize that current alkaline extraction techniques are unable to distinguish such non-biogenic amorphous fractions from biogenic amorphous Si and non-biogenic fractions could be a substantial component of extracted Si in some soils where non-biological amorphous Si fractions dominate. ASi as such refers to all Si that is released during alkaline extraction, while BSi only refers to the biogenic fraction. A reliable, yet easily performed method that could distinguish between both biogenic and lithogenic amorphous fractions of Si, would be a great asset to our understanding of the ecosystem BSi reservoir.

It is also likely that micro-organisms will impact the dissolution and/or the retention of BSi in ecosystem soils. Microbial communities influence a range of different soil functions, including organic matter decomposition, nitrogen fixation, carbon fixation and related trace gas fluxes (Conrad 1996). Bacterial microfilms have been associated with the formation of secondary Fe- and Al-silicates and bacteria are well-known to impact diatom BSi dissolution in coastal ecosystems (Bidle et al. 2003), by removing organic coatings from diatom frustules in seawater. A similar role is likely important in the terrestrial biosphere, especially when physical dissolution fluxes are slowed down due to high ambient DSi concentrations. Fungi could play a similar role, with fungi playing a key role in the weathering of mineral silicates (Bonneville et al. 2009). Still, we know of no studies that have investigated effects of either fungi or microbial communities on terrestrial ecosystem soil BSi storage.

4.7.3 Hydrology

Hydrology by definition controls water fluxes through ecosystems and hence the potential DSi export. The terrestrial biosphere can be seen as a series of interconnected spatially distributed subsystems. These subsystems are distributed both horizontally (adjacent ecosystems, uplands and wetlands…) and vertically (litter, soil, sediment, bedrock…) and hydrology mediates material fluxes between the different subsystems.

Although dust-related transport of silica exists between terrestrial and ocean ecospheres, this is only a minor fraction of BSi in the terrestrial biosphere, with the major part of ecosystem BSi either dissolving into soil water or remaining buried in ecosystem soils. The impact of hydrology is even more intricate if one considers that recycling of BSi to DSi is positively correlated to ambient DSi concentration. Longer water residence time will allow higher DSi concentrations to develop in soil water and will slow down the actual dissolution processes. Ground water table and hydrology also partly control ecosystem biodiversity and hence impact on potential DSi uptake into the biological BSi buffer. Hydrologists have already taken advantage of the fact that different flowpaths produce distinct Si concentrations, and have therefore used DSi as a hydrologic tracer (e.g. Hornberger et al. 2001).

Quantification and qualification of flow paths of DSi through ecosystems via different hydrological pathways (leaching, surface flow, lateral flows) should be coupled to ecosystem BSi balances. This is a necessary prerequisite to understand the residence time of BSi in ecosystem soils. The effect of hydrology on BSi storage and recycling within soils could be addressed by focusing on hydrological gradients within ecosystems and by conducting experiments artificially impacting hydrology, thus providing an understanding how changing flow paths will alter BSi storage in ecosystems.

Addressing issues of the influence of hydrology will allow us to quantify key factors that land cover changes have on Si fluxes. For example, impervious cover in urban landscapes has been shown to alter the base-flow to surface run-off ratio as well as increased erosion in urban landscapes. Understanding changing hydraulic pathways is essential to increase our understanding of ecosystem silica buffering with human alteration of landscapes (see key control anthropogenic influences).

4.7.4 Mineral weatherability

The weatherability of parent rock and soil mineral silicates will determine how much DSi is available for external input into the ecosystem. On a global scale lithology is an important component describing Si fluxes. Weathering of silicate minerals is prime input for Si into the biological reservoirs.

Recent research has e.g. shown that tropical vegetation can differ in isotopic Si content, depending on the weathering stage of the parent material, indicating a direct link between vegetation Si and weathered Si (Henriet et al. 2008). Impacts of morphoclimate zonation on the size of the ecosystem BSi reservoir is expected :weathering rates and weathering stage differ between tropical and temperate regions. Cornelis et al. (2010b) hypothesize a tight link between weathering and Si fluxes from the soil-plant system, reviewing existing literature in an exhaustive way. Further studies are especially needed in soil-plant systems at high latitudes, as global change will most strongly impact temperature, hydrology and vegetation in these regions (Cornelis et al. 2010b), and in systems with high weathering rates, since most studies focused on the biological control on Si cycling and export in highly weathered tropical systems with a low availability of mineral-derived Si.

4.7.5 Anthropogenic influences

We hypothesize that anthropogenic disturbances in landscapes will strongly impact the ecosystem BSi processing, as they will affect the key factors identified here. In a natural world, ecosystem BSi is everywhere. For example, a typical West-European floodplain would consist of a mosaique of deciduous forest, grasslands, heathlands, with wetlands in the riverine floodplain. In the current anthropocene, man-made ecosystems appear, such as croplands and pastures, and urban landscapes with roads, villages and cities. Natural ecosystems are now only isolated BSi hot-spots. In the new ecosystems, uptake of BSi into the soil BSi reservoir will be absent or reduced since urban areas have limited ability to take up DSi into vegetation, cropland and pastures have reduced soil accumulation, and BSi in vegetation is removed frequently through harvesting. Increased soil erosion in deforested areas can result in the loss of the bio-active soil layers and remove the high BSi concentrations found in surficial soils. Human land use also changes hydrological flow paths, by increasing surface flows, decreasing precipitation infiltration and increasing river canalization. Changes in precipitation patterns as expected with climate change (increased importance of event-like, intense precipitation) will increase surface run-off and top-soil erosion, potentially strongly reducing BSi rich surface soils.

The spatial distribution of BSi hotspots in the landscape is important to BSi storage and recycling. Riparian wetlands, for example, have a well-known buffering effect on the nitrogen and phosphorus cycle, but also on the silica cycle (Struyf & Conley 2009). The age of the ecosystems will equally be an important factor with older systems building up a significant BSi reservoir in soils, which might differ strongly in function and biomass from younger, less developed ecosystems.

Whether human land use impacts will induce a net increase or reduction of silica fluxes depends on the combination of key controls we identified. This change adds to other anthropogenic impacts on silica fluxes through the riverine continuum. Important reductions in riverine Si transport have been observed by deposition in reservoirs. Damming of rivers leads to increased trapping of BSi in the lake sediments, reducing downstream transport of Si (Humborg et al. 1997).

4.7.6 Implications

Silica budget studies that do not incorporate the influence terrestrial of biological Si storage and processing to estimate Si fluxes, could seriously be biased in deducting origin and size of silica fluxes and the associated carbon sinks. We realize such recent studies are currently based on best available knowledge: increasing knowledge on the mechanisms of the ecosystem Si filter, and quantifying its importance in global Si budgets, is therefore essential to avoid potential bias. Accurately quantifying human influence on the ecosystem silica filter is also necessary in models of coastal productivity. An estimate of past Si fluxes to the coastal zone is impossible without a good concept of biological Si buffering along the land-ocean continuum. As small changes in nutrient input parameters can have complex results for productivity, incorporating knowledge on the ecosystem Si buffer in models for continental Si mobilization could shed new light on our concept of eutrophication and associated shifts in coastal phytoplankton (Cloern, 2001). The same holds true for the carbon pump in the ocean, which is controlled by the burial of diatoms in the deep ocean.

The silica-associated carbon pump partly is dependent upon the annual input of terrestrial Si into the coastal zone and eventually the ocean

We encourage research focusing on our 5 key topics – ecosystem biodiversity, BSi dissolution rates and reactivity, hydrology, weatherability of silicate minerals and anthropogenic landscape impacts – to better quantify the global and local importance of the terrestrial biogeochemical Si cycle, and especially the ecosystem Si filter. Research focusing on the five key topics, both individually or on synergetic effects, will allow us to constrain the timescales at which biological Si storage and recycling is occurring, its persistence and reactivity throughout the soil profile, its dependence on ecological processes, its feedbacks to hydrology, its interaction with man's activities and ultimately its global relevance in silica budgets.

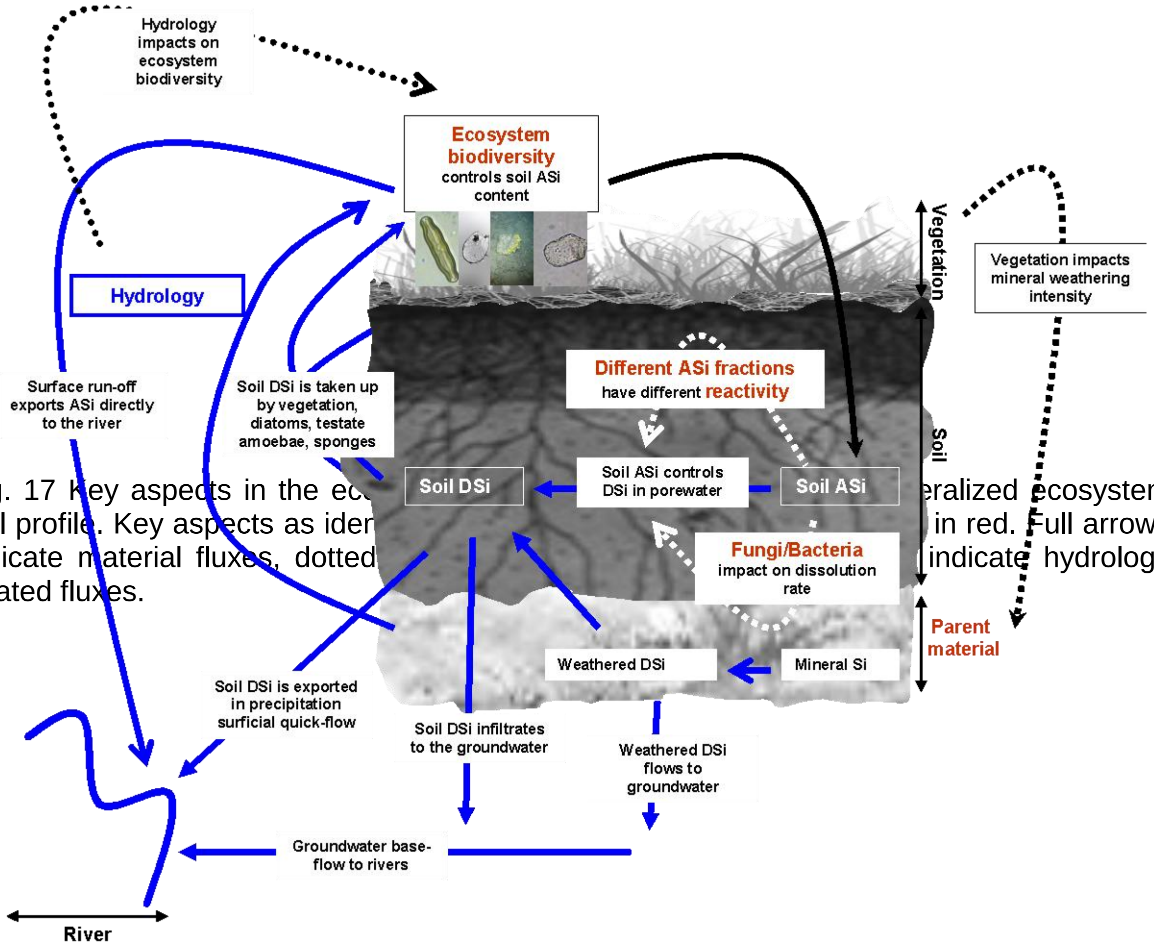


Fig. 17 Key aspects in the ec eralized ecosystem soil profile. Key aspects as iden in red. Full arrows indicate material fluxes, dotted indicate hydrology related fluxes.

5. Policy support

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 will improve their quality with respect to eutrophication in rivers and the coastal zone: the prediction capacity for eutrophication events will increase. As such, organizations such as OSPAR and the EU in general can benefit from our results. We will provide all data in ready-to-use datasets to MUMM (Management Unit of the North Sea Mathematical Models), for public archiving.

- 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 BSi and DSi. Once implemented in biogeochemical models, our data will provide valuable input for the integrated management of watersheds

Recommendations

- incorporation of the analysis of DSi and BSi in regular monitoring networks, e.g. VMM. Our data shows the important human impact on Si fluxes. Si is an important water quality parameter, and its incorporation will both ensure a dataset to test and improve our proposed conceptual model, and to evaluate the effect of management options in watersheds.
- To incorporate Si as an important human influenced parameter in conservation objectives for ecosystems. Such conservation objectives can be based on ecosystem services delivered by ecosystems, such as a healthy Si-N-P ratio in output water. Si was successfully implemented in e.g. the conservation objectives for the Scheldt estuary.
- To use our results in the communication to the public about the importance of a green natural network and also reforestation for attaining sustainable good water quality. Our results are a primary example of the far-reaching effects deforestation can have, even as far as water quality in estuaries and coastal zones
- To arrange a specific call within BELSPO targeting integrated nutrient budgets on the catchment scale. This could center on studies that map spatial and temporal variability of nutrient cycling, and on interactions between vegetation, micro-organisms, abiotic variables and intensity of biogeochemical nutrient cycling. Research at local spatial scales (e.g. treatment wetlands, riparian wetlands, macrophytes patches) and in chronosequences provides essential information on hot-spots and hot-moments. This research can then be applied for optimal restoration at the landscape scale. In this context, a focus on integration of different nutrient cycles is crucial but has currently been lacking.
- To use our results to show policy makers that we should intensify policies to encourage reforestation, and discourage further deforestation. Our results emphasize that deforestation impacts quality of adjacent internationally important water bodies (Scheldt estuary, North Sea) in more ways than traditionally assumed (e.g. increased erosion, decreased C-uptake).

6. Dissemination and valorisation

6.1 Valorisation

We will provide all data in ready-to-use datasets to MUMM (Management Unit of the North Sea Mathematical Models), for public archiving. This will allow incorporation of our data in scientifically under build management of watersheds.

We disseminated our results in several scientific forums of global and more local importance, and presented a key note on our study on the Goldschmidt meeting in 2010 in Knoxville, one of the most important yearly meetings of the geochemical scientific community.

Our results have been published, have been submitted or will be submitted in/to both specialized biogeochemical peer-reviewed journals and broad-public scientific peer-reviewed journals.

Our results have received attention in popular scientific magazines and broad-public media.

We have maintained a regularly updated website through the whole of the project.

6.2 Scientific conferences

Struyf E., Conley D.J. (2008) Silica: an essential nutrient in wetland biogeochemistry. Isotopes in biogenic silica (IBIS) meeting, Oxford Brookes University, 16 May 2008.
Invited oral presentation.

Struyf E., Conley D.J. (2008) Silica: an essential nutrient in wetland biogeochemistry. SWS European Chapter Meeting. Wetlands and climate change : new challenges for wetland research. Kuressaare, Estonia. 29 June – 3 July 2008. Oral presentation.

Struyf E., Conley D.J., Meire P., Kokfelt U. (2009) Silica: an essential nutrient in wetland biogeochemistry. Wetland connections. Joint meeting of the Society of Wetland Scientists and the Wetland Biogeochemistry Symposium. Madison, Wisconsin, USA, 22-26 June 2009. Oral presentation

Struyf E., Kokfelt U., Smis A., Conley D.J., Humborg C., Mörth C.-M., Vandevenne F., Meire P. Interactions between climate change, land use and the biological silica buffer in wetlands and forests. Isotopes in biogenic silica (IBIS) meeting, Swansea University, UK, 8-9 February, 2010. Invited oral presentation

Struyf E. et al. The silica dynamics of deforestation: new evidence for a biologically controlled Si cycle. EGU meeting, Vienna, May 2010. Oral presentation

Struyf E., Kokfelt U., Smis A., Conley D.J., Humborg C., Mörth C.-M., Vandevenne F. & Meire P. Interactions between climate change, land use and the biological silica buffer in wetlands and forests. Keynote at Goldschmidt conference, Earth, Energy and the Envionment. Knoxville, USA, 13-18 June 2010. Invited keynote.

Clymans, W., Govers, G., Struyf, E., Van Damme, S., Van Wesemael, B., Langhans, C., Van den Putte, A. and Meire, P., 2009. Mobilisation of Amorphous and Dissolved Silica on Small Agricultural Plots. Geophysical Research Abstracts, 11. EGU meeting 2009

Clymans, W., Govers, G., Struyf, E., Van Damme, S., Van Wesemael, B. and Meire, P., 2009. Limitations of the Amorphous Silica Analysis for Runoff Sampling. Geophysical Research Abstracts, 11. EGU meeting 2009

Clymans, W., Frot, E., Govers, G., Struyf, E., Smis, A., Vandamme, S., Van Wesemael, B., Meire, P., 2010. Comparing the silica pathways through small agricultural and forested catchments. Geophysical Research Abstracts, 12. EGU meeting 2010

6.3 Seminars

Clymans, W., Frot, E., Govers, G., Struyf, E., Smis, A., Vandamme, S., Van Wesemael, B., Meire, P., 2010. Comparing the silica pathways through small agricultural and forested catchments. 4th Belgian Geography Days – Geography in a changing world

Clymans, W., 2010. The effect of land use changes on the terrestrial silica cycle. Geology Science Seminar 2010, GeoBioSphere Centre, Lund University, Sweden.

7. Publications

7.1 Peer-reviewed publications

Struyf E., Conley DJ. (2009) Silica: an essential nutrient in wetland biogeochemistry. Frontiers in Ecology and Environment, 7(2), 88-94. ISI IF: 6.92

Van Damme S., Dehairs F., Tackx, M., Beauchard O., Struyf E., Gribsholt B., Van Cleemput O. & Meire P. (2009) Tidal exchange between a freshwater tidal marsh and an impacted estuary; the Scheldt estuary, Belgium". Estuarine Coastal & Shelf Science, 85, 197-207. ISI IF: 1.97

Struyf E., Smis A., Van Damme S. , Meire P. & Conley D.J. (2010) The global biogeochemical silicon cycle. Silicon, 1, 207-213.

Struyf E., Smis A., Van Damme S., Garnier J, Govers G.,Van Wesemael B., Conley D.J., Batelaan O., Frot E., Clymans W., Vandevenne F., Lancelot C., Goos P. & Meire P (2010). Historical land use change has lowered terrestrial silica mobilization. Nature communications, 1,129. doi:10.1038/ncomms1128

Smis A., Van Damme S., Struyf E. , Govers G., Van Wesemael B., Clymans W., Frot E., Van Hoestenberghe T. & Meire P. 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. Biogeochemistry, in press

Struyf E., Kotowski W., Jacobs S., Van Damme S., Opdekamp W., Backx H. & Meire P. Tracing Si-N-P ecosystem-pathways: is relative uptake in riparian vegetation influenced by soil moisture, mowing management and species diversity? Hydrobiologia, in press

Vandevenne F., Meire P. & Struyf E. Agricultural silica harvest: have man created a new and important loop in the global silica cycle. Submitted to Frontiers in Ecology and the Environment

Struyf E. & Conley D.J. Emerging understanding of the ecosystem silica buffer. Submitted to Biogeochemistry

Clymans, W., Govers, G., Struyf, E., Van Damme, S., Van Wesemael, B., Meire, P., 2010. Amorphous silica analysis in terrestrial runoff samples. Submitted to Geoderma

8. Acknowledgements

We would like to acknowledge all follow-up committee members for their input.

We thank BELSPO for the great research opportunities LUSi provided.

Thanks to all people who assisted during the installation of the field sites.

Thanks to VMM and WHL for the cooperation during sampling in rain events.

Thanks to all the farmers who allowed us to perform research on their land.

Thanks to STATUA for all the statistical support.

Thanks to Lund University for providing the opportunity to cooperate on Swedish soils.

Thanks to all TIMOTHY (BELSPO SSD Project) members for the tight cooperation.

Thanks to MUMM and VLIZ for providing database opportunities.

Thanks to FWO for funding research that build on our LUSi results.

Thanks to David Cox, our helping hand at BELSPO!

9. References

Aoki Y, Hoshino M & Matsubara T (2007) Silica and testate amoebae in a soil under pine-oak forest. Geoderma, 142: 29-35.

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

Bidle KD, Brzezinski MA, Long RA, Jones JL & Azam F (2003) Diminished efficiency in the oceanic silica pump caused by bacteria-mediated silica dissolution. Limnol Oceanogr, 48: 1855-1868.

Bonneville S, Smits MM, Brown A, Harrington J, Leake JR, Brydson R & Benning LG (2009) Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. Geology, 37: 615-618.

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

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochemical Cycles 16: 1121

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.

Conrad R (1996) Soil microorganisms as controllers of atmospheric trace gases (H2, CO, CH4, OCS, N2O and NO). Microbiol Rev, 60: 609.

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

Cornelis J-T, Delvaux B, Georg RB, Lucas Y, Ranger J & Opfergelt S (2010b) Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: a review. Biogeosciences Discuss, 7: 5873-5930Datnoff LE, Snyder GH and Korndörfer GH. 2001. Silicon in Agriculture. Elsevier.

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

Epstein E (2009) Silicon: its manifold roles in plants. Ann Appl Biol, 155: 155-160.

Gérard, F., Mayer, K. U., Hodson, M. J. & Ranger, J. (2008) Modelling the biogeochemical cycle of silicon in soils: Application to a temperate forest ecosystem. Geochimica et Cosmochimica Acta, 72, 741-758.

Gressel J. 2008. Transgenics are imperative for biofuel crops. Plant Science 174: 246-263.

Henriet C, De Jaeger N, Dorel M, Opfergelt S & Delvaux B (2008) The reserve of weatherable primary silicates impacts the accumulation of biogenic silicon in volcanic ash soils. Biogeochemistry, 90: 209–223.

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

Hornberger GM, Scanlon TM & Raffensperger JP (2001) Modelling transport of dissolved silica in a forested headwater catchment: the effect of hydrological and chemical time scales on hysteresis in the concentration-discharge relationship. Hydrol Process, 15: 2029-2038.

Humborg C, Ittekkot V, Cociasu A & Von Bodungen B (1997) Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386: 385-388.

Jugdaohsingh R, Anderson SHC, Tucker KL, Elliott H, Kiel DP, Thompson RPH and Powell JJ. 2002. Dietary silicon intake and absorption. Am J Clin Nutr 75: 887–93.

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

Kokfelt U, Struyf E & Randsalu U (2009) Diatoms in peat – Dominant producers in a changing environment? Soil Biol Biochem, 41: 1764-1766.

Kokfelt U, Struyf E., Reuss N., Sonesson M, Rundgren M, Skog G., Rosén P & Hammarlund D (2010) Wetland development, permafrost history and nutrient cycling inferred from late Holocene peat and lake sediment records in subarctic Sweden. J Paleolimnol, 44: 327-342.

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

Loucaides S, Van Cappellen P & Behrends T (2008) Dissolution of biogenic silica from land to ocean: role of salinity and pH. Limnol Oceanogr, 53: 1614-1621.

Ma J.F., Miyake Y. & Takahashi E., 2001. Silicon as a beneficial element for crop plants. In: Silicon in agriculture. Datnoff L.E., Snyder G.H. & Korndörfer G.H. (eds), Elsevier Science., 2001

Massey FP, Ennos AR & Hartley SE (2007) Grasses and the resource availability hypothesis: the importance of silica-based defences. J Ecol, 95: 414-424.

Massey FP, Smith MJ, Lambin X & Hartley SE (2008) Are silica defences in grasses driving vole population cycles? Biol Letters, 4: 419-422.

McLaren JR & Turkington R (2010) Ecosystem properties determined by plant functional group identity. J Ecol, 98: 459-469.

Meunier J.D., Guntzer F., Kirman S. & Keller C., 2008. Terrestrial plant-Si and environmental changes. Mineralogical Magazine 72: 263-267

Schoelynck J, Bal K, Backx H, Okruszko T, Meire P & Struyf E (2010) Silica uptake in aquatic and wetland macrophytes: a strategic choice between silica, lignin and cellulose? New Phytol, 186: 385-391.

Sommer M, Kaczorek D, Kuzyakov Y & Breuer J (2006) Silicon pools and fluxes in soils and landscapes - a review. J Plant Nutr Soil Sc, 169: 310-329.

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, Van Damme S. and Meire P. 2004. Possible effects of climate change on estuarine nutrient fluxes: a case study in the highly nutrified Schelde estuary (Belgium, The Netherlands). Estuar. Coast. Shelf Sci. 60: 649–661

Struyf E, Van Damme S, Gribsholt B, Middelburg JJ & Meire P (2005) Biogenic silica in freshwater marsh sediments and vegetation. Mar Ecol Prog Ser, 303, 51-60.

Struyf E., Conley DJ. (2009) Silica: an essential nutrient in wetland biogeochemistry. Frontiers in Ecology and Environment, 7(2), 88-94.

Struyf E, Opdekamp W, Backx H, Jacobs S, Conley DJ & Meire P (2009) Vegetation and proximity to the river control amorphous Si storage in a riparian wetland (Bierbza National Park, Poland). Biogeosciences, 6: 623-631.

Struyf E., Smis A., Van Damme S. , Meire P. & Conley D.J. (2010a) The global biogeochemical silicon cycle. Silicon, 1, 207-213.

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.

Van Cappellen P, Dixit S & van Beusekom J (2002) Biogenic silica dissolution in the oceans: Reconciling experimental and field-based dissolution rates. Global Biogeochem Cy, 16: 10.

Van Dyck K, Van Cauwenbergh R, Robberecht H, Deelstra H. 1999. Bioavailability of silicon from food and food supplements. Fresenius J Anal Chem 363: 541–4.

Wang H L, Brown S L, Magesan G N, Slade AH, Quintern M, Clinton PW, Payn TW. 2008. Technological options for the management of biosolids. Environ Sci Pollut Res 15, 308-317