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Retention of dissolved silica within the fluvial system of the conterminous USA

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Abstract Dissolved silica (DSi) is an important nutrient in aquatic ecosystems. Increased DSi retention within the fluvial system due to damming and eutrophication has led to a decrease in DSi exports to coastal waters, which can have severe consequences for coastal areas where ecosystem functioning depends on fluvial DSi inputs. The analysis of fluvial DSi fluxes and DSi retention at regional to global scales is thus an important research topic. This study explores the possibility to empirically assess regional DSi retention based on a spatially explicit estimation of DSi mobilization and fluvial DSi fluxes calculated from hydrochemical monitoring data. The uncertainty of DSi retention rates (r_{DSi}) estimated for particular rivers is high. Nevertheless, for the St. Lawrence River (r_{DSi} = 91 %) and the Mississippi River (r_{DSi} = 13 %) the estimated DSi retention rates are reasonable and are supported by literature values. The variety of sources of the uncertainty in the DSi retention assessment is discussed.

Keywords Dissolved silica · Rivers · Retention · Land–ocean matter transfer · Biogeochemistry · Silicon cycle

Abbreviations

A_{AA}	Areal proportions of artificial areas (= urban + industrial areas)
A_{AL}	Areal proportion of agricultural land
A_{BF}	Areal proportion of broadleaved forests
A_{CF}	Areal proportion of coniferous forests
A_{HV}	Areal proportion of herbaceous vegetation (= grasslands)
A_{SL}	Areal proportion of shrublands
BSi	Biogenic, amorphous silica
COV	Coefficient of variance
DSi	Dissolved silica
F_{DSi}	Total fluvial DSi flux
f_{DSi}	Specific fluvial DSi flux
$f_{DSi,calc}$	F_{DSi} calculated from hydrochemical monitoring data
$f_{DSi,mob}$	Spatially explicit estimates of DSi mobilization
q	Mean annual runoff

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r_{DSi} DSi retention rate
$T_{air,mean}$ Mean air temperature

Introduction

Dissolved silica (DSi) is an important nutrient in terrestrial and aquatic ecosystems (e.g. Conley 2002; Conley et al. 1993). Its primary source is the weathering of silicate minerals (e.g. Derry et al. 2005; Bluth and Kump 1994). The land–ocean transfer of DSi through rivers is an important part of the global silica cycle. For most coastal areas, the fluvial export of silica is the main source of this nutrient (e.g. Meybeck et al. 2007; Treguer et al. 1995).

Rivers are not just conduits between the terrestrial and the marine system. A proportion of the terrestrial DSi is retained within the fluvial system due to biotic uptake, mainly by diatoms, and net-losses of biogenic, amorphous silica (BSi) to sediments. It is estimated that 16 % of the bioavailable silica (DSi + BSi) exported to the coasts are contributed by BSi, mainly in the form of diatoms (Conley 1997).

Eutrophication and construction of dams and locks increase DSi retention and subsequently decrease DSi exports (e.g. van Bennekom and Salomons 1981; Conley et al. 1993; Humborg et al. 2008; Friedl et al. 2004). The anthropogenic contributions of nitrogen and phosporous enhance the diatom growth, which leads to decreasing DSi concentrations in freshwater systems (e.g. Schelske and Stürmer 1971; Hartmann et al. 2011). The construction of dams and locks fosters diatom growth due to the increased water residence times, and leads to intensive sedimentation and net-losses of silica to the sediments within the reservoirs (e.g. Garnier et al. 1999; Koch et al. 2004; van Bennekom and Salomons 1981). These effects have become known as the "artificial lake effect" (van Bennekom and Salomons 1981) and were discussed specifically with regard to larger impoundments (e.g. Humborg et al. 1997). Recent studies showed that also smaller impoundments can be significant silica sinks (Humborg et al. 2006). For the Baltic Sea, for instance, Humborg et al. (2008) estimated a decrease in fluvial DSi inputs of 30–40 % over the last 100 years due to eutrophication and damming.

While for N and P, anthropogenic inputs compensate for the retention of these nutrients in the fluvial system, there is no significant replenishement for DSi (Humborg et al. 2000). Thus, eutrophication increases the fluvial exports of N and P, but decreases the export of DSi. The resulting shift in nutrient concentrations in coastal waters may change the algae species composition to the disadvantage of diatoms, which are a key species in functioning marine ecosystems (Officer and Ryther 1980). Moreover, these changes may increase the frequency of harmful blooms of non-diatom phytoplankton like noxious dinoflagellates (Danielsson et al. 2008; Humborg et al. 2000; Officer and Ryther 1980; Smayda 1990).

Fluvial DSi fluxes vary substantially among different rivers, with consequences for the receiving coastal zones. The spatial variability of total fluvial DSi exports to the coasts were assessed at the global scale by Dürr et al. (2011) and Beusen et al. (2009). Both studies were based on historical river chemistry data from the mouths of large rivers, representing rather pristine states. Therefore, effects of anthropogenically enhanced DSi retention were avoided. In these studies, the DSi mobilization from the terrestrial system into the rivers was not assessed directly, as it can be expected that the fluvial transport of DSi was impacted by natural DSi retention in lakes and wetlands (Dürr et al. 2011). The global land–ocean silica transfer and its anthropogenic disturbance was recently assessed in a box model approach (Laruelle et al. 2009). This model included silica mobilization to rivers, silica retention within the fluvial system, and fluvial exports of silica to the coasts, however, without representation of their spatial variability.

Spatial patterns and first order controls of terrestrial DSi exports to fluvial systems were investigated at regional to continental scale for North America and Japan (Jansen et al. 2010; Moosdorf et al. 2011; Hartmann et al. 2010). These studies used empirical models to predict the DSi mobilization from geodata of lithology and runoff. The spatially resolved model outputs ('spatially explicit estimates') allow identifying areas with higher and lower contributions to fluvial DSi fluxes (Moosdorf et al. 2011). Moosdorf et al. (2011) applied the empirical model from Jansen et al. (2010) to predict the long-term average annual DSi mobilization into the fluvial system of North America. The model was trained on river catchments throughout the conterminous USA, chosen to be preferably small and to lack lakes. DSi retention in these fluvial systems was assumed to be negligible and, consequently, the observed fluvial fluxes of DSi were assumed to represent the DSi mobilized from the terrestrial system (Jansen et al. 2010).

These studies highlighted the small scale heterogeneity of DSi mobilization and identified areas with disproportionally high contributions to the land–ocean DSi fluxes. For example, small river catchments in near coast, per-humid mountainous areas with mafic volcanic lithology were shown to be hot-spots (Hartmann et al. 2010), i.e. areas with area specific fluvial DSi fluxes of more than ten times the world average (after Meybeck et al. 2006). Thus, a proper assessment of the retention effects on the fluvial DSi exports requires the representation of the spatial DSi mobilization patterns.

DSi retention has mainly been assessed for individual lakes and reservoirs using direct mass balance approaches (e.g. Schelske 1985; Cook et al. 2010; Hofmann et al. 2002; Triplett et al. 2008; Garnier et al. 1999). Fluvial DSi fluxes distinguishing DSi mobilization and DSi retention were assessed for a small number of rivers applying a deterministic model (Riverstrahler model; for the Seine River (France) by Sferratore et al. 2005; the Luleälven and Kalixälven Rivers (Sweden) by Sferratore et al. 2008; for the Red River (Vietnam/China) by Le Thi et al. 2010). At the regional scale, Humborg et al. (2008) investigated statistic relations between DSi yields from tributary rivers of the Baltic Sea and catchment characteristics which can be related to DSi retention. These studies demonstrated a strong negative influence of lakes and reservoirs on fluvial DSi exports to the coastal zones.

At the global scale, three studies exist which give estimates of DSi retention within the fluvial system (Laruelle et al. 2009; Beusen et al. 2009; Dürr et al. 2011). Laruelle et al. (2009) presented a global mass balance model developed from a systematic literature review. According to this model, 469 Mt SiO_2 a^{-1} of DSi enter the fluvial system from terrestrial sources while the fluvial export of DSi amounts to only 373 Mt SiO_2 a^{-1}. The discrepancy of 96 Mt SiO_2 a^{-1} represents the net-conversion of DSi to BSi within the fluvial system. Of this BSi, a part is buried in the sediments (i.e. the actual retention), while the other part is exported to the coasts.

Beusen et al. (2009), who modelled natural fluvial DSi fluxes, gave a first-order estimate of anthropogenically induced DSi retention within large reservoirs to obtain an estimate of the contemporary, anthropogenically impacted fluvial DSi exports. For this, they assumed DSi retention rates to equal that of dissolved inorganic phosphorous after Harrison et al. (2005) (18 % at global scale) or that of sediments after Vörösmarty et al. (2003) (19 % at global scale).

Dürr et al. (2011) assumed natural DSi retention within lakes and wetlands of 16 ± 8 % and a anthropogenically induced DSi retention within reservoirs of 6 ± 3 % as long-term averages. In this first-order estimate, they assumed an annual retention of 20 ± 10 g SiO_2 per m^2 of lake area (Campy and Meybeck 1995) as representative for all natural lakes and reservoirs; for wetlands the silica retention per area was assumed to be 15 % of that in lakes (Dürr et al. 2011).

There is a need for regional to continental scale studies which empirically assess the DSi retention. It is however unknown if available data are suitable for such analyses. This study investigates the possibilities of an approach to asses DSi retention in the fluvial system of the conterminous USA, combining highly resolved, spatially explicit estimates of DSi mobilization into streams and rivers (Moosdorf et al. 2011) and fluvial DSi fluxes calculated from hydrochemical monitoring data. Theoretically, this approach would offer the advantage to derive empirically based estimates of the amount of DSi retained in the fluvial system during the lateral land–ocean transfer at a regional scale. It could also provide the opportunity to reveal spatial differences in DSi retention which could be empirically analyzed with regard to potential controlling factors. These hypothesized advantages of the approach presented here are tested and evaluated.

Methods and data

Data processing

Hydrochemical monitoring data (Alexander et al. 1997; USGS 2009) from 624 sampling locations (Fig. 1), particularly DSi concentration and instantaneous discharge, and long-term average annual runoff from the UNH/GRDC data set (Fekete et al. 2002) were used to calculate long-term average annual fluvial DSi fluxes. The UNH/GRDC runoff data set

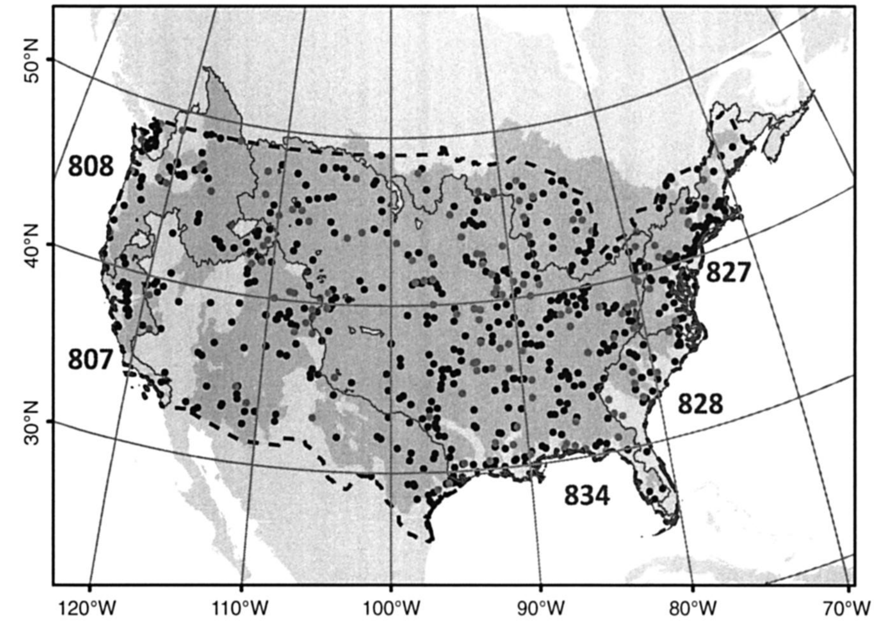


Fig. 1 USGS sampling locations used in the analyses; the *dark grey area* represents the monitored area addressed by this study, and the *grey points* represent the sampling locations used by Jansen et al. (2010). The *dashed line encircles* the conterminous USA. The *straight grey lines* delineate the tributary areas of coastal segments after Meybeck et al. (2006). The *numbers* stand for 'San Francisco Coast' (807), 'South Cascadia Basin' (808), 'New England Coast' (827), 'Blake-Nares Basin' (828), and 'North Mexican Gulf' (834)

is a global, spatial data set (grid cells, resolution 0.5°) which combines long-term discharge gauging data with climate-driven water balance model outputs. The gauging data provided certain information on the long-term average annual runoff from river basins while the model outputs were used to derive the spatial heterogeneity of runoff within the river basins (Fekete et al. 2002).

The sampling locations were selected following four criteria:

1) DSi concentrations and instantaneous discharge measurements were available for at least twelve consecutive months,
2) The sampling location could be positioned on the stream network represented by the digital elevation model (DEM) used (hydrosheds DEM by Lehner et al. 2008, 15" resolution),
3) The computed catchments were consistent with USGS meta data (20 % maximum deviation between reported and computed catchment areas) and satellite imagery (visual check), and
4) The UNH/GRDC runoff data set gave a long-term average annual runoff of more than 0 mm a^{-1}.

For the Mississippi River, only sampling locations upstream of the diversion at the Old River outflow channel (cf. Goolsby et al. 1999) were considered, because diversions are not depicted in the stream network derived from a digital elevation model. Artificial waterways and streams and rivers directly influenced by water diversion were omitted for the same reason.

As many non-overlapping series of twelve consecutive monthly measurements as possible were identified from the time series of each sampling location (on average 3.3 twelve-month-series per station). The averages of DSi concentrations were then weighted by the instantaneous discharge measurements. Based on the computed catchment boundaries and geodata (Table 1), catchment properties like land cover, climate, and areal proportions of lakes were calculated. For all geodata processing, the software ArcGIS 9.3 (ESRI^{TM}) was used.

Long-term averages of annual runoff were derived from the UNH/GRDC runoff composites (Fekete et al. 2002), a spatial raster data set with 0.5° resolution. To assure runoff values are available for the whole terrestrial area considered, the runoff rasters were extended by one raster cell, each new cell assigned the average runoff of the adjacent cells. Note that UNH/GRDC runoff is based on discharge gauging data covering time series comprising at least twelve years in the time span 1960–1990; the exact time spans covered by the time series differ (Fekete et al. 2002). However, it is assumed that the runoff data are representative long-term averages for that period. River chemistry data refer to samples taken between 1967 and 2007.

Table 1 Geodata used for deriving catchment properties

Parameter	Source	Resolution
Lithology	Lithological map of North America v1.0 (Jansen et al. 2010)	Based on geologic maps 1:500,000 to 1:5,000,000
Land cover	GlobCover (Arino et al. 2007), reclassified after Jansen et al. (2010)	10″
Lakes	SRTM water body data set (NASA/NGA 2003)	Based on SRTM DEM with 3″ resolution
Runoff	UNH/GRDC runoff (Fekete et al. 2002)	30′
Climate	WorldClim (Hijmans et al. 2005)	30″
DEM derived flow directions	Hydrosheds (Lehner et al. 2008)	15″
DSi mobilization into streams	Moosdorf et al. (2011)	1.4 km^2
Population density (1990)	Gridded population of the world v3 (CIESIN 2005)	2.5′

Land cover information was derived from the GlobCover data set (Arino et al. 2007) that is based on remote sensing data (MERIS) between 2004 and 2006. Lake area was taken from the SRTM Water Body data set (NASA/NGA 2003). This data set represents all standing water bodies of a size of at least 0.1 km^2 (at least 600 m length and 183 m width) in February 2000, as they were derived from remote sensing data (Landsat TM5, SRTM derivatives) (NASA/NGA 2003). These water bodies comprise natural lakes as well as reservoirs and larger ponds. It is assumed that this state of water body distribution is fairly representative for the time since the 70's and, thus, the time span covered by the hydrochemical data, because most dams have already been created earlier (Graf 1993).

Estimation of DSi retention

DSi retention (Eq. 1) was calculated from the specific fluvial fluxes of DSi ($f_{DSi,calc}$), which were derived from USGS hydrochemical data and UNH/GRDC runoff data, and the spatially explicit estimates of DSi mobilization from Moosdorf et al. (2011) ($f_{DSi,mob}$). These DSi mobilization estimates are based on the empirical model from Jansen et al. (2010), which was trained on a set of river catchments throughout the study area. These 'training catchments' were selected to be preferably small and lack lakes, so that it could be assumed that retention of DSi within the freshwater system of these catchments is rather negligible (Jansen et al. 2010). The empirical model was trained on observed DSi fluxes, which were calculated similar to the procedure applied in this study, and which were assumed to equal the DSi mobilization from the terrestrial system in these training catchments. Of the 624 catchments considered by this study, 140 belong to these training catchments.

Thus, for the training catchments, $f_{DSi,mob}$ represents an estimate on the area specific, fluvial DSi flux at the catchments outlet. For catchments not used as training catchments, a significant DSi retention is more likely, because catchments are larger and/or contain lakes and reservoirs which theoretically increase DSi retention rates. It is hypothesized that for these 'non-training catchments', there is a tendency for $f_{DSi,mob}$ being higher than $f_{DSi,calc}$ due to DSi retention.

$$r_{DSi} = \left(f_{DSi,mob} - f_{DSi,calc}\right) / f_{DSi,mob} \quad (1)$$

$f_{DSi,calc}$ long-term annual fluvial flux of DSi calculated from USGS hydrochemical data (t SiO_2 km^{-2} a^{-1}).
$f_{DSi,mob}$ estimated long-term annual DSi mobilization from the terrestrial system into the fluvial system (t SiO_2 km^{-2} a^{-1})

Total DSi retention within the study area was calculated from the average specific DSi mobilization within the entire monitored area (Fig. 1) and an area-weighted average $f_{DSi,calc}$ from a subset of 161 catchments that cover the entire monitored area without overlaps ('non-overlapping catchments'). Of these non-overlapping catchments, 121 could be apportioned to the tributary areas of distinct coastal segments of the conterminous USA (according to the classification after Meybeck et al. 2006; Fig. 1). We applied this method to calculate estimates of DSi retention rates within the fluvial system of these distinct tributary areas and the fluvial DSi exports to the respective coastal segments. For the segmentation of the coastlines we referred to the classification of Meybeck et al. (2006), but derived a new delineation of the tributary areas based on the stream network of the Hydrosheds DEM (Lehner et al. 2008). The coastal segments after Meybeck et al. (2006) relevant for our study area are 'San Francisco Coast', 'South Cascadia Basin', 'New England Coast', 'Blake-Nares Basin', and 'North Mexican Gulf' (Fig. 1).

DSi retention rates calculated for each individual catchment were analyzed for statistical correlations (Pearson correlations) with catchment properties and hydrochemical characteristics that might show a potential influence on DSi retention. Note that Pearson correlations address linear relationships only, while functional relationships are often non-linear (cf. Reshef et al. 2011). Thus, potential relationships between DSi retention rates and hydrochemical or catchment parameters were further checked by visual scatter-plot analysis. For all statistical analysis the software Statistica 9 (Statsoft®) was utilized.

Results

Estimates of DSi retention

The calculation of DSi retention rates (DSi retention relative to the estimated DSi mobilization) for individual catchments resulted in negative values for a substantial part of the considered river catchments (282 of 624). The spatial distribution of estimated DSi retention per catchment is characterized by a regional clustering with negative retention estimates dominating the western region of the study area and positive retention estimates in the eastern part (Fig. 2). Some values of estimated DSi retention are given in Table 2, including the three largest of the basins considered here (Mississippi R., Colorado R., and St. Lawrence R.) and two more catchments within the St. Lawrence River Basin partly covering the Great Lakes (St. Mary's R. and Detroit R.).

The empirical mobilization equation, derived by Jansen et al. (2010) and applied spatially explicitly to North America by Moosdorf et al. (2011), gives an average DSi mobilization of 1.65 t SiO_2 km^{-2} a^{-1} and a total DSi mobilization of 13.1 Mt SiO_2 a^{-1} into streams and rivers of the conterminous USA. Within the monitored area considered here (Fig. 1), the estimated DSi mobilization amounts to 10.9 Mt SiO_2 a^{-1}. For the catchments representing this area without overlaps ('non-overlapping catchments', $n = 161$), a fluvial DSi flux of 9.4 Mt SiO_2 a^{-1} was calculated, which represents the long-term average annual fluvial export of DSi from the monitored area. Assuming the total estimated DSi mobilization and the total calculated fluvial DSi export as representative for this area, a total retention of 1.4 Mt SiO_2 a^{-1} or 13 % of the DSi mobilized into streams and rivers is calculated.

Of the 161 non-overlapping catchments, 121 can be apportioned to tributary areas of distinct coastal segments of the conterminous USA (after Meybeck et al. 2006) (Table 3; Fig. 1). The proportions of these tributary areas covered by the monitored area considered here range from 36 % (Blake-Nares Basin) to 94 % (North Mexican Gulf). The number of non-overlapping catchments representing the monitored area within each tributary area ranges from seven (San Francisco Coast) to 47 (New England Coast). Based on the apportioned catchments, DSi retention rates for these tributary areas could be calculated as was done for the entire monitored area.

The calculated DSi retention rates per tributary area range from a highly negative estimate of −84 % (San Francisco Coast) to a positive estimate of 20 % (New England Coast). Regardless of whether the calculated DSi retention rates are reasonable estimates of the DSi retention within the fluvial system or they just represent a technical discrepancy between the estimated DSi mobilization and the observed fluvial DSi export, they can be applied as correction factors to deduce a regionalized estimate of the total fluvial DSi exports to the coastal segments based on the estimated DSi mobilization (Table 3). While for the New England Coast these regionalized estimates of fluvial DSi exports are close to the values previously reported by Dürr et al. (2011), the estimates of fluvial DSi exports to the San Francisco Coast, the Blake-Nares Basin, and the North Mexican Gulf are substantially lower than the values reported by Dürr et al. (2011) (Table 3).

DSi retention per catchment and its potential factors

Potential controlling factors of DSi retention can be factors which increase the biotic DSi uptake, e.g. the availability of other nutrients, or factors which increase the burial of BSi in sediments, particularly the abundance of lake areas. The hydrochemical and catchment properties considered here as potential controlling factors are interpreted in this regard. The 'training catchments', which were used by Jansen et al. (2010) to fit the DSi mobilization model, were selected to be rather pristine, small, and lacking

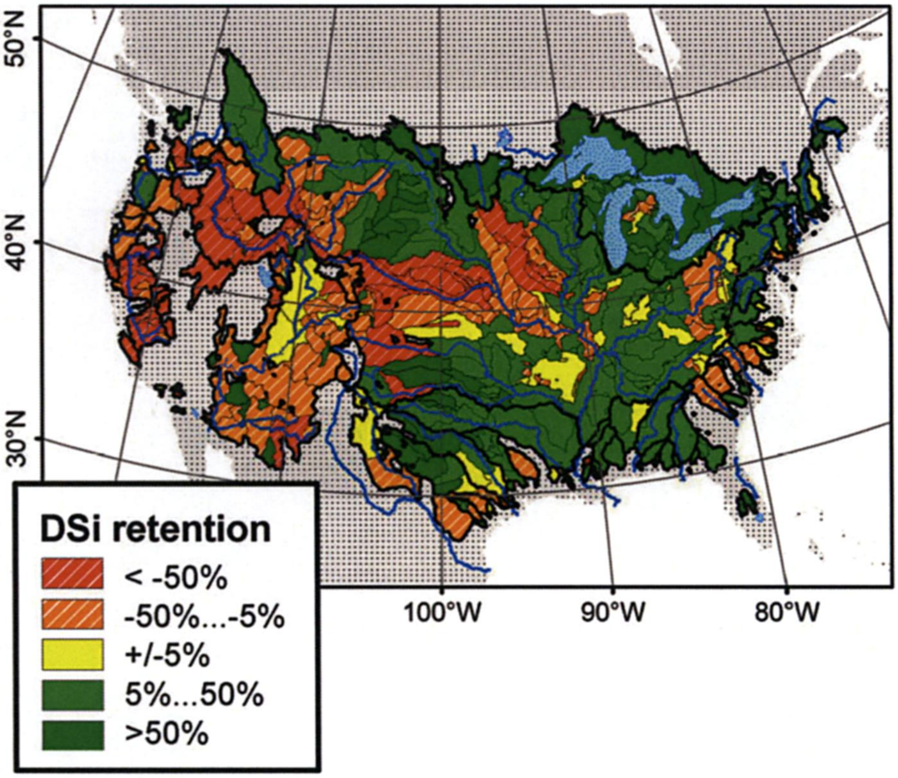


Fig. 2 Estimated DSi retention, calculated for each catchment (Eq. 1)

Table 2 Examples for estimated DSi retention, relative and in g SiO_2 m^{-2} lake area a^{-1}

Sampling location	12-month-series	Catchment area (km^2)	Lake area prop. (%)	DSi retention	
				Relative to $f_{DSi,mob}$[a] (%)	(g SiO_2 m^{-2} a^{-1})[b]
Mississippi at Vicksburg	3	2,914,988	0.9	13	18.8
Colorado above Morelos Dam near Andrade	10	615,827	0.3	−28	−21.0
St. Mary's River	2	209,316	43.9	67	3.3
Detroit River	1	592,720	37.1	81	3.5
St. Lawrence River at Cornwall	1	771,620	34.7	91	4.3

[a] DSi retention rate relative to estimated DSi mobilization from terrestrial system

[b] Refers to lake area within each catchment

riverine lakes, so that DSi retention within the fluvial system of these catchments could be assumed to be minimal (Jansen et al. 2010). In the following analysis, it is therefore distinguished between catchments previously used as 'training catchments' by Jansen et al. (2010) ($n = 140$) and the remaining 'non-training catchments' ($n = 484$).

The DSi retention estimated per catchment is on average negative for the training catchments as well as the non-training catchments, with a very similar mean of −7.6 and −7.5 %, respectively. The estimated DSi retention shows a strong negative correlation with DSi concentration, for both the training and the non-training catchments (Table 4; Fig. 4a, b). For the

Table 3 DSi mobilization into streams and rivers, fluvial DSi exports, and DSi retention in inland waters per tributary areas of coastal segments (COSCAT segmentation scheme after Meybeck et al. 2006)

COSCAT-Sea basin			Monitored Area					Entire COSCAT area		Dürr et al. (2011)	
ID	Name	Area[a] (tsd. km^2)	N	Areal prop. (%)	$F_{DSi,mob}$ (Mt SiO_2 a^{-1})	$F_{DSi,calc}$ (Mt SiO_2 a^{-1})	r_{DSi} (%)	$F_{DSi,mob}$ (Mt SiO_2 a^{-1})	$F_{DSi,corr}$ (Mt SiO_2 a^{-1})	Area[b] (tsd. km^2)	F_{DSi} (Mt SiO_2 a^{-1})
807	San Francisco Coast	201	7	63	0.31	0.57	−84	0.39	0.72	252	2.37
808	South Cascadia Basin	759	20	80	2.46	2.75	−12	3.35	3.75	836	4.45
827	New England Coast	546	47	48	0.86	0.69	20	1.99	1.60	579	1.46
828	Blake-Nares Basin	305	16	36	0.25	0.26	−4	0.68	0.71	452	1.67
834	North Mexican Gulf	3,709	31	94	5.26	4.55	14	5.89	5.09	3,685	9.56

ID original ID of coastal segments and their tributary area used by Meybeck et al. (2006)

[a] Area of the tributary areas recalculated based on the Hydrosheds DEM (Lehner et al. 2008)

[b] Area of the tributary area according to the original COSCAT data set (Meybeck et al. 2006) used by Dürr et al. (2011), which is based on the simulated topographic network at 30′ resolution (STN 30; Vörösmarty et al. 2000; Fekete et al. 2001)

N number of 'non-overlapping catchments' representing the monitored area considered by this study; *Areal* areal proportion of the monitored area considered in this study per COSCAT tributary area prop., $F_{DSi,corr}$ fluvial DSi export to coastal segment as a regionalized estimate based on the estimated DSi mobilization (Moosdorf et al., 2011) and corrected by the DSi retention rate r_{DSi}, see text

training catchments, for which $f_{DSi,mob}$ is an estimate of the specific fluvial DSi flux assuming minimal DSi retention, this correlation is likely due to the fact that the mobilization equation tends to underestimate specific fluxes with high DSi concentrations and overestimate specific DSi fluxes with low DSi concentrations (Jansen et al. 2010). However, the negative correlation between DSi concentration and estimated DSi retention is similar within the non-training catchments (Table 4; Fig. 4a, b). Note that the statistical distribution of mean DSi concentrations per catchment is similar for both subsets of catchments (Table 6). The strong negative correlation between DSi concentration and DSi retention estimates are further visible in the similar spatial patterns of high DSi concentrations and negative DSi retention estimates (Figs. 2, 3). As the same runoff data were used for the calculation of $f_{DSi,calc}$ and the estimation of $f_{DSi,mob}$, there is no significant correlation between DSi retention estimates and runoff (Table 4).

Because it was expected that biotic uptake and retention of DSi increase with catchment size and areal proportion of lakes, these parameters were expected to show significant correlations to estimated DSi retention. For example, for the Great Lakes (St. Lawrence R., Detroit R., St. Mary's R. in Table 2) the lake effects became indeed clearly visible. However, catchment size and lake area proportion were not found to be statistically related to the estimated DSi retention per catchment (Table 4; Fig. 4c–f). One reason for the lack of relationship is that for most of the catchments considered in this study areal proportions of lakes are rather low (90th percentile = 2 %). Thus, the set of river catchments analyzed here is probably less suitable to analyze correlations between lake area proportions and DSi fluxes compared with the river catchments draining to the Baltic Sea studied by Humborg et al. (2008) (90th percentile of lake area proportion = 10 %).

As it is hypothesized that biotic uptake and retention of DSi (r_{DSi}) increases with the availability

Table 4 Correlation matrix: estimated DSi retention per catchment versus catchment characteristics and water quality parameters for all catchments and different subsets of catchments[a]

Set of catchments (c.)	DSi retention (r_{DSi})							
	All c.		Training c.		Non-training c.		Non-overl. c.	
Parameter	*N*	*r*	*N*	*r*	*N*	*r*	*N*	*r*
Catchment size (m^2)	624	0.02	140	−0.16	484	0.02	161	0.06
$\log_{10}$[Catch. size (m^2)]	624	−0.07	140	−0.10	484	−0.07	161	−0.02
q (mm a^{-1})	624	0.06	140	0.14	484	0.04	161	0.07
DSi conc. (μmol L^{-1})	624	**−0.68**	140	**−0.70**	484	**−0.68**	161	**−0.64**
$f_{DSi,calc}$ (t SiO_2 $km^{-2}a^{-1}$)	624	**−0.27**	140	−0.13	484	**−0.30**	161	**−0.22**
$f_{DSi,mob}$ (t SiO_2 $km^{-2}a^{-1}$)	624	**0.08**	140	0.13	484	0.07	161	0.13
Air temperature (°C)	624	**0.15**	140	−0.03	484	**0.20**	161	0.13
Population density (1990) (persons km^{-2})	624	0.06	140	0.09	484	0.07	161	0.01
Agricultural lands (1)	624	0.01	140	**−0.22**	484	0.07	161	0.03
Broadleaved forest (1)	624	**0.19**	140	0.16	484	**0.20**	161	0.11
Coniferous forest (1)	624	**−0.14**	140	0.16	484	**−0.22**	161	−0.03
Shrublands (1)	624	**−0.15**	140	−0.06	484	**−0.16**	161	**−0.25**
Grasslands (1)	624	0.01	140	**−0.28**	484	**0.09**	161	0.08
Artificial areas (1)	624	**0.09**	140	0.12	484	**0.10**	161	0.06
Lake area proportion (1)	624	0.04	140	0.05	484	0.04	161	0.13
Water temperature (°C)	613	0.05	138	−0.07	475	0.07	159	−0.02
SPM conc. (mg L^{-1})	496	−0.03	115	**−0.24**	381	0.04	131	**−0.28**
pH	614	−0.03	138	−0.14	476	−0.01	159	0.02
NO_2^- + NO_3^- conc. (μmol L^{-1})	603	**−0.10**	136	**−0.19**	467	−0.08	157	−0.04
TP conc. (μmol L^{-1})	600	−0.06	135	−0.01	465	**−0.10**	157	**−0.32**

q runoff, *SPM* suspended matter, *TP* total phosphorous

[a] Correlations which are significant to the $p = 0.05$ level are highlighted in bold font

of N and P, it was expected that the concentrations of these nutrients would show a positive correlation to r_{DSi}. However, there are only low and negative correlations or no statistically significant correlations between these nutrient concentrations and r_{DSi} (Table 4).

For the non-training catchments, there is a low but significant correlation between estimates of DSi retention and mean annual air temperature ($r = 0.199$, $p = 0.000$, Fig. 4h). This correlation is due to catchments with high DSi concentrations and highly negative DSi retention estimates, which to a larger proportion show lower mean air temperatures (Fig. 4h). If catchments with DSi concentrations higher than 200 μmol L^{-1}, i.e. roughly the upper quartile of all catchments (188 μmol L^{-1}), are discarded from the analysis, the correlation becomes insignificant ($n = 371$, $r = 0.091$, $p = 0.080$). With regard to DSi retention within the fluvial system, land cover could be a potential factor controlling water quality and thus indirectly controlling diatom growth and sedimentation. Indeed, there are statistically significant but low correlations between land cover and estimated DSi retention. However, because no correlations with potential water quality parameters were found, the indirect effects from land cover on DSi retention cannot be identified sufficiently in this study.

Recent studies reported a land-use-related perturbation of terrestrial silica pools, with an increase in DSi mobilization to streams and rivers after deforestation (Carey and Fulweiler 2011; Clymans et al. 2011; Conley et al. 2008), which can switch to a decrease in DSi mobilization after soil BSi storages are depleted in the course of sustained cultivation (Struyf et al. 2010a). As land use effects were not taken into account in the DSi mobilization model of

Table 5 Examples for silica retention within lakes, reservoirs, and whole rivers from the literature

Lake/River	Silica retention		Reference (Method)
	g SiO_2 $m^{-2}a^{-1}$	rel. (%)	
Oligotrophic lakes with crystalline catchment	<10	–	Campy and Meybeck (1995) (compilation from literature)
Volcanic lakes + partially mesotrophic lakes	>20	–	
Lake Mead (Colorado R.)	28.5	13	After Kelly (2001) (based on DSi fluxes, inflow, outflow)
Lake Powell (Colorado R.)	16.4	8	
Falcon reservoir (Rio Grande)	26.6	17	
Amistad reservoir (Rio Grande)	−76.0	−66	
Lower Columbia River reservoirs	–	−20	
Lake St. Croix (Mississippi R.)	–	10	Triplett et al. (2008) (mass balance of DSi and BSi, inflow, outflow)
Lake Pepin (Mississippi R.)	–	20	
Lake Michigan	3.0	80	Schelske (1985) after Parker et al. (1977) (mass balance DSi + BSi, inflow, atmospheric deposition, outflow, permanent loss to sediments)
Lake Superior	3.6	65	Schelske (1985) after Johnson and Eisenreich (1979) (mass balance DSi + BSi, inflow, outflow, atmospheric deposition, shoreline erosion, sediment deposition, silicate authigenisis, redissolution from sediments)
Lake Texoma (Red River, USA)	22.2	30	This study (mass balance based on DSi concentrations and instantaneous discharge from USGS data at inflows and outflow)
Marne reservoir (Seine River basin)	–	48	Garnier et al. (1999) (mass balance of DSi inflows and outflows, based on three year time series)
Aube reservoir (Seine River basin)	–	57	
Seine reservoir (Seine River basin)	–	43	
Seine River in 2001 (wet year)	–	9	Sferratore et al. (2006) (mass balance based on DSi and BSi measurement from different sampling locations, atmospheric inputs, estimates of anthropogenic point sources)
Seine River in 2003 (dry year)	–	6	
Red River (China/Vietnam)	–	23	Le Thi et al. (2010) (based on Seneque/Riverstrahler model)
Lower lakes (Murray River, Australia)	–	39	Cook et al. (2010) (mass balance, DSi inflows and outflows)
Lake Biwa (Japan)	30	80	Goto et al. (2007) (mass balance, DSi inflows and outflows)

Jansen et al. (2010), such effects could influence the over/-underprediction of DSi mobilization and thus the derived DSi retention rates. However, correlations between land cover classes and r_{DSi} in this study are low and do not allow to draw such a conclusion.

Discussion

Comparison with literature values

In this study, for the conterminous USA a total DSi retention of 1.4 Mt SiO_2 a^{-1} or 13 % of the estimated

Table 6 Average physiographic properties derived from different geodata sets, averages of DSi concentrations, calculated DSi fluxes, and estimated DSi mobilization

Subset of catchments	N	Mean	Min	Max	10th Perc.	90th Perc.	SD
Catchment size (km^2)							
Training catchments	140	3,963	8.45	37,891	113	11,335	7,583
Non-training catchments	484	54,003	0.34	2,914,988	110	100,737	201,079
Areal proportion of lakes							
Training catchments	140	0.002	0	0.03	0	0.004	0.004
Non-training catchments	484	0.012	0	0.439	0	0.023	0.035
Monitored area[a]		0.048[a]					
Runoff (mm a^{-1})							
Training catchments	140	340	0	2,308	41	626	301
Non-training catchments	484	308	0	1,793	12	657	267
Monitored area[a]		217	0	2,681	0	545	261
Mean DSi concentration (μmol L^{-1})							
Training catchments	140	159	24	781	70	244	108
Non-training catchments	484	162	8	761	77	305	107
Monitored area[a]		109[b]					
$f_{DSi,calc}$ (t SiO_2 $km^{-2}a^{-1}$)							
Training catchments	140	2.61	0	19.98	0.49	4.35	2.64
Non-training catchments	484	2.5	0	26.98	0.11	5.41	2.82
Monitored area[a]		1.42[c]					
$f_{DSi,mob}$ (t SiO_2 $km^{-2}a^{-1}$)							
Training catchments	140	2.57	0	19.03	0.48	4.01	2.6
Non-training catchments	484	2.47	0	48.87	0.13	4.39	3.42
Monitored area[a]		1.63	0	82.27	0	3.812	2.96
Mean air temperature (°C)							
Training catchments	140	9.4	−2.3	20.5	2.0	18.1	5.5
Non-training catchments	484	10.2	−0.9	22.4	4.5	17.2	4.7
Monitored area[a]		10.0	−7.9	23.4	3.8	17.4	5.2

[a] For the monitored area, statistics of estimated DSi mobilization, runoff, and air temperature refer to the raster data sets

[b] Was derived as flux-weighted average of DSi concentration of the 161 non-overlapping catchments

[c] Was derived as catchment area-weighted average of $f_{DSi,calc}$ of the 161 non-overlapping catchments

DSi mobilization was calculated. Literature values to which our results can, under restrictions, be compared are the first-order estimates given by Beusen et al. (2009) and Dürr et al. (2011).

Beusen et al. (2009) estimated a DSi retention rate of 21–22 % for the entire North American continent. This DSi retention refers only to the anthropogenically induced DSi retention in large reservoirs (dams of at least 15 m height); unperturbed DSi retention and DSi retention within natural lakes and smaller reservoirs are not taken into account. Our study focuses on the total DSi retention, including the natural, unperturbed DSi retention in lakes. Further, our study concentrates on the conterminous USA that represents the southern, more populated and developed part of North America. We expect that within our study area, the anthropogenically induced DSi retention in reservoirs is above the North American average. Regarding these considerations, our DSi retention estimate seems rather low compared to that of Beusen et al. (2009).

Beusen et al. (2009) assumed DSi retention rates in large reservoirs to equal the retention rates of dissolved inorganic phosphorous (DIP) as estimated by Harrison et al. (2005). A literature review suggests

Table 7 Average lithologic and land cover composition of different sets of catchments

Subset of catchments (c.)	Training catchments		Non-training catchments		Monitored area
N	140		484		
	Mean	Std.	Mean	Std.	Mean
Lithology					
Unconsolidated sediments	0.21	0.34	0.21	0.29	0.24
Siliciclastic sedimentary rocks	0.34	0.35	0.31	0.29	0.33
Mixed sedimentary rocks	0.08	0.17	0.07	0.13	0.08
Carbonate rocks	0.19	0.29	0.16	0.26	0.13
Metamorphic rocks	0.08	0.19	0.11	0.22	0.06
Basic and intermediate plutonics	0.00	0.02	0.01	0.03	0.01
Acid plutonics	0.05	0.16	0.05	0.12	0.04
Basic volcanics and pyroclastic rocks	0.04	0.12	0.04	0.11	0.04
Acid and intermediate volcanics	0.02	0.09	0.03	0.09	0.03
Land cover					
Agricultural land	0.18	0.21	0.18	0.18	0.20
Broadleaved forest	0.35	0.28	0.34	0.24	0.31
Coniferous forest	0.26	0.30	0.23	0.25	0.16
Shrubland	0.03	0.08	0.07	0.13	0.10
Grassland	0.17	0.15	0.16	0.12	0.18
Urban area	0.00	0.00	0.01	0.04	0.00
Other land cover than listed above	0.00	0.01	0.02	0.04	0.05

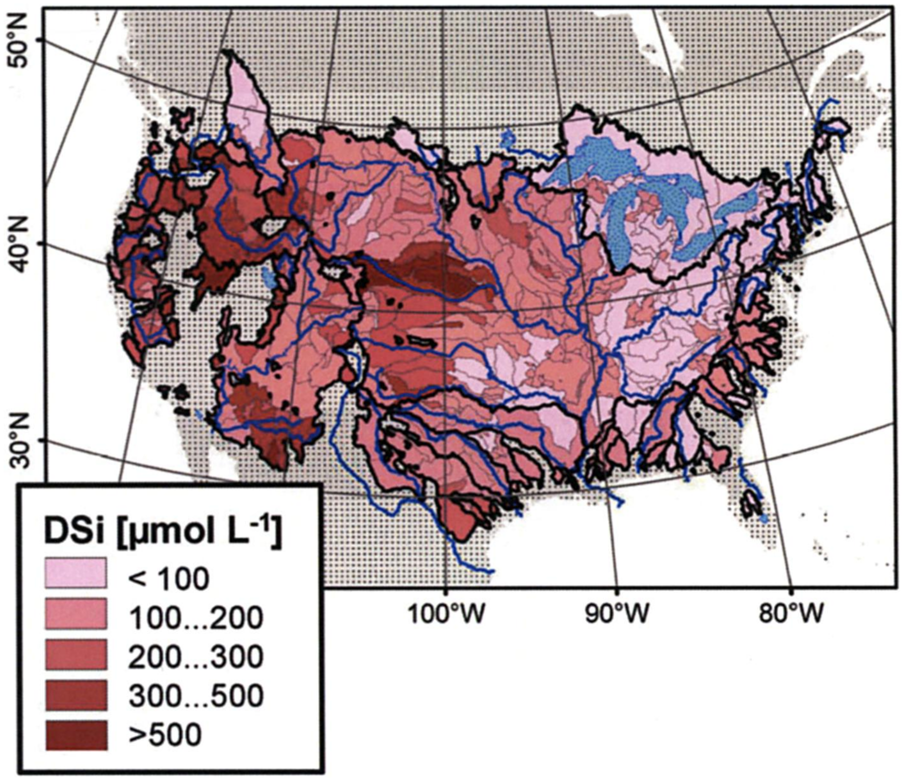


Fig. 3 Average DSi concentrations derived from hydrochemical monitoring data, averages are weighted by instantaneous discharge

that this assumption likely leads to an overestimation of DSi retention in reservoirs. Studies investigating retention of DSi as well as DIP indicate that retention rates of DIP are generally higher. Mass balances of dissolved matter within five reservoirs in the western USA gave retention rates for DSi that are at least 2.5 times lower than that of DIP in each case (Kelly 2001). DIP retention rates that are substantially higher than DSi retention rates were also reported for the highly perturbed Red River (China/Vietnam) (Le Thi et al. 2010; factor 2.3), a semiarid riverine lake systems in Australia (Cook et al. 2010; factor 2.0), and three reservoirs in the upper Seine Basin (Garnier et al. 1999; factors 1.1–1.7). No studies reporting DSi retention rates higher than that of DIP are known to the authors.

For a first-order estimate of the total DSi retention in lakes and reservoirs, Dürr et al. (2011) applied the average annual silica retention per lake area of 20 ± 10 g SiO_2 m^{-2} a^{-1} reported by Campy and Meybeck (1995). If we applied this value to our study area (total lake area of 321 10^3 km^2), we would obtain a total DSi retention of 6.4 ± 3.2 Mt SiO_2 a^{-1}, i.e. several times higher than our estimate of 1.4 Mt SiO_2 a^{-1}. However, for extensive lake areas as the North American Great Lakes the expectable DSi retention rates are lower than that of lakes on average (see below). If we excluded the St. Lawrence river basin with the Great Lakes from this calculation (total remaining lake area of 53.4 10^3 km^2), we would obtain a total DSi retention of 1.1 ± 0.5 Mt SiO_2 a^{-1}, i.e. still several times higher than the 0.28 Mt SiO_2 a^{-1} calculated for this area by our method. If we relate our estimates of total DSi retention to the lake area, we get an average silica retention of 4.3 g SiO_2 m^{-2} a^{-1} (total study area) or 5.8 g SiO_2 m^{-2} a^{-1} (excluding St. Lawrence River basin with the Great Lakes), which is substantially lower than the lake average given by Campy and Meybeck (1995).

For the particular examples of the Great Lakes, the DSi retention rates estimated in this study are very close to that reported by Schelske (1985) (Tables 3, 5). For the St. Mary River basin, which comprises Lake Superior, a DSi retention of 67 % or 3.3 g SiO_2 m^{-2} a^{-1} (refers to lake area) was estimated here. In his mass balance comprising fluvial fluxes of DSi and BSi as well as atmospheric inputs after Johnson and Eisenreich (1979), Schelske (1985) estimated a silica retention of 65 % or 3.6 g SiO_2 m^{-2} a^{-1} for Lake Superior.

The DSi retention of 18.8 g SiO_2 m^{-2} a^{-1} in lakes and reservoirs estimated here for the Mississippi River Basin (referring to the sampling location at Vicksburg, Mississippi) is well within the range of DSi retention calculated for Lake Texoma (mass balance solely based on USGS data), Lake Mead, Lake Powell, and the Falcon Reservoir (after Kelly 2001) and the average DSi retention within lakes after Campy and Meybeck (1995) (Table 5). This suggests that the DSi retention estimated for the Mississippi River is reasonable.

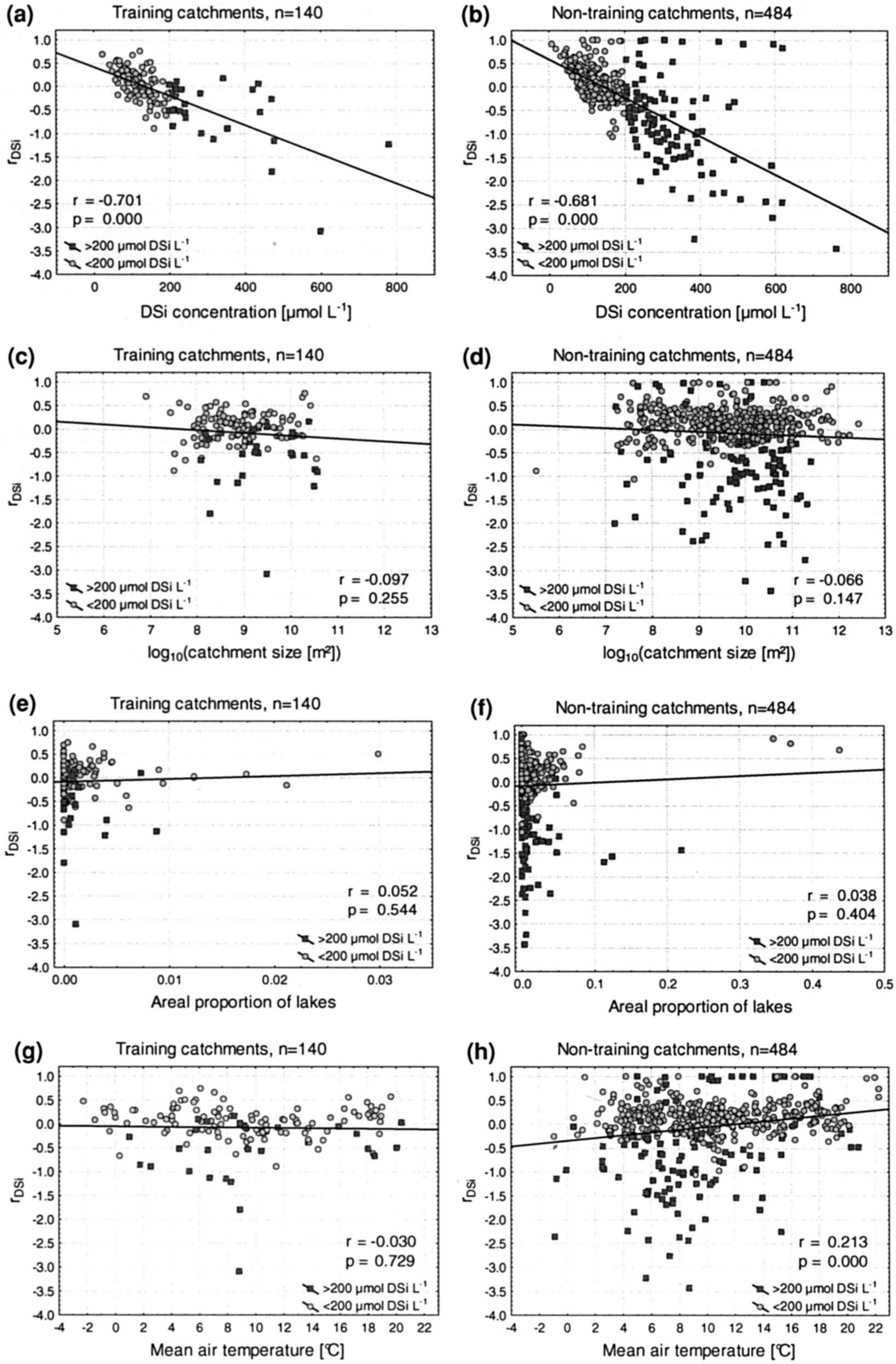
The Mississippi River catchment and the St. Lawrence River catchment are the two largest in our study area and comprise about 55 % of the total area and 92 % of the lake area. They contribute about 54 % of the total runoff, 47 % of the total estimated DSi mobilization from the terrestrial system to streams and rivers, and 37 % of the fluvial DSi export calculated from hydrochemical monitoring data. For the remaining part of the monitored area, the total estimated DSi mobilization (5.7 Mt SiO_2 a^{-1}) is lower than the calculated fluvial DSi export (5.9 Mt SiO_2 a^{-1}), which results in a negative estimate of DSi retention of −4 % relative to the DSi mobilization. While for the catchments of the Mississippi River and the St. Lawrence River our retention estimates can be supported by literature values, we have to conclude that for the remaining part of the study area we underestimate DSi retention on average due to an underestimation of the actual DSi mobilization. Thus, we conclude that the estimated DSi retention of 13 % within the entire study area is underestimated as well.

Uncertainties due to methods

The uncertainties of DSi retention estimates are the sum of the uncertainties related to estimation of DSi mobilization and calculation of fluvial DSi fluxes. They may further be related to additional sources of DSi not addressed here, the non-availability of BSi data at a regional scale, and the steady state assumptions that might not be valid for the investigated systems. These issues are addressed in the following subsections.

Calculation of DSi fluxes

Uncertainties in the calculation of fluvial DSi fluxes depend on uncertainties and the representativeness of the hydrochemical data and runoff data used for flux


(a)
Training catchments, n=140
r = -0.701
p = 0.000
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
DSi concentration [μmol L⁻¹]
(b)
Non-training catchments, n=484
r = -0.681
p = 0.000
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
DSi concentration [μmol L⁻¹]
(c)
Training catchments, n=140
r = -0.097
p = 0.255
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
log10(catchment size [m²])
(d)
Non-training catchments, n=484
r = -0.066
p = 0.147
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
log10(catchment size [m²])
(e)
Training catchments, n=140
r = 0.052
p = 0.544
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
Areal proportion of lakes
(f)
Non-training catchments, n=484
r = 0.038
p = 0.404
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
Areal proportion of lakes
(g)
Training catchments, n=140
r = -0.030
p = 0.729
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
Mean air temperature [℃]
(h)
Non-training catchments, n=484
r = 0.213
p = 0.000
>200 μmol DSi L⁻¹
<200 μmol DSi L⁻¹
Mean air temperature [℃]
rDSi

◀ **Fig. 4** Scatter-plots of estimated DSi retention r_{DSi} (Eq. 1) versus catchment properties and hydrochemical properties, subsets with mean DSi concentrations higher than 200 µmol L^{-1}, corresponding to roughly the upper quartile of 188 µmol L^{-1}, are plotted as *dark squares*

calculations. DSi fluxes calculated from series of monthly measurements have specific uncertainties as well as a positive bias (Stelzer and Likens 2006). The uncertainty is related to the interannual variability of total DSi fluxes and the question how well the seasonality in DSi concentrations is represented by the time-series considered. This uncertainty decreases with increasing sampling frequency (Stelzer and Likens 2006) and with the length of the times series considered. Positive biases are likely to occur, because short-termed peak-flows, that are characterized by decreased DSi concentrations (also cf. Hornberger et al. 2001), may not be captured by the sampling frequency but are present in the runoff data (Stelzer and Likens 2006).

The hydrochemical data set used here is based on a monthly sampling, with on average 3.3 twelve-month-series per sampling location. For 136 of the sampling locations, only one twelve-month-series was retrieved. For the 488 sampling locations with two or more twelve-month-series, the average DSi concentration for distinct twelve-month-series shows an average coefficient of variance (COV) of 12.0 %. The coefficient of variance represents the standard deviation expressed as percentage relative to the mean value. Here, it offers valuable clues on the interannual variation of average DSi concentrations, but also on the certainty with which the average DSi concentration of one particular twelve-month-series represents the long-term average DSi concentration. The average COV gives a hint to the certainty with which the long-term annual DSi fluxes calculated for sampling locations with only one twelve-month-series of DSi measurements match the actual long-term DSi fluxes.

For 10 % of the 488 sampling locations with more than one twelve-month average DSi concentration, the COV is lower than 2.55 %, for 90 % it is lower than 24.8 %. However, there is no significant correlation between the number of twelve-month-series and the COV of annual mean DSi concentration ($r = 0.07$, $p = 0.119$). Moreover, the COV of mean DSi concentrations calculated for distinct twelve-month-series is positively correlated to the COV of the annual means of the instantaneously measured discharge ($r = 0.495$, $p = 0.000$). These findings confirm that uncertainties in long-term DSi flux calculations are especially high for intensively fluctuating discharges, which are predominantly found in semi-arid regions in the western half of the conterminous USA (Stelzer and Likens 2006).

It has to be expected that, due to the positive bias, fluvial DSi fluxes are likely overestimated in this study. For a sampling frequency of 28 days, which is close to that of the monthly data used here, Stelzer and Likens (2006) estimated this bias to be about 13 % on average for twenty river catchments distributed throughout the conterminous USA. This value is expected to be representative for the study area, at least for river catchments of the size used by Stelzer and Likens (2006). Their river catchments, ranging from 0.13 to about 696 km^2 in size (Stelzer and Likens 2006), are however small compared to those used in this study (average size: 3,963 km^2 for training catchments, 54,003 km^2 for non-training catchments, Table 6). Because the bias increases with the temporal variability of the discharge (Stelzer and Likens 2006), and because this temporal variability of discharge can be expected to be lower in large rivers with extensive catchments, the bias for the catchments used in this study is probably lower. As the empirical DSi mobilization model from Jansen et al. (2010) was derived from calculated DSi fluxes of the training catchments, the positive bias of the calculated DSi fluxes is as well inherent in the DSi mobilization estimates.

UNH/GRDC runoff data, which we used for the DSi flux calculation, can be considered to represent the long-term annual runoff well within our study area, because these data are derived from long-term discharge gauging data covering at least twelve years of discharge measurements per station and because the conterminous USA is well covered by those gauging stations (Fekete et al. 2002). Because the runoff was routed over a stream network with 30' resolution (STN 30) and only gauging stations with contributing areas of at least 10,000 km^2 were considered (Fekete et al. 2002), the data are expected to be more uncertain for river catchments of less than 10,000 km^2. However, as the same runoff data were used for the estimation of DSi mobilization (Jansen et al. 2010; Moosdorf et al. 2011) and calculation of DSi fluxes from hydrochemical data, no direct impact of uncertainties in the runoff data on the DSi retention estimate is expected.

Furthermore, the same is true for uncertainties in the delineation of catchments. The same catchment delineations were used to calculate the average DSi mobilization and the average UNH/GRDC runoff per catchment. Thus, the maximum tolerated deviation of 20 % between the catchment size reported by the USGS and that calculated in this study has no direct effect on the estimated DSi retention.

Estimates of DSi mobilization

Within the training catchments, the DSi mobilization estimation raster from Moosdorf et al. (2011) explained 89 % of the variance of calculated DSi fluxes. This variance was explained by the predictors runoff and lithology. Other potential factors of DSi mobilization not included in the respective mobilization function, i.e. temperature, land cover, slope gradient, and physical denudation rates, were discussed by Jansen et al. (2010). Uncertainties due to the spatially explicit application and the extrapolation to the entire North American continent were discussed by Moosdorf et al. (2011).

Moosdorf et al. (2011) give a DSi mobilization estimate for entire North America that is 22 % lower than that given by Beusen et al. (2009) and still 6 % lower than the fluvial DSi export estimated by Dürr et al. (2011). The lower DSi mobilization used here is a probable reason for the comparatively low calculated DSi retention. For the area represented by the training catchments, the spatially explicit estimation by Moosdorf et al. (2011) gives a total DSi flux of 0.89 Mt SiO_2 a^{-1}, while the total flux of DSi calculated from hydrochemical monitoring data amounts to 0.97 Mt SiO_2 a^{-1}. Thus, the estimates by Moosdorf et al. (2011) underestimate the total fluvial DSi flux by 8.6 % within the area, for which retention of DSi was assumed to be negligible and thus DSi fluxes were assumed to represent the DSi mobilized from the terrestrial system into the fluvial system (Jansen et al. 2010).

Note that Jansen et al. (2010) fitted their DSi mobilization model based on the calculated specific DSi fluxes ($f_{DSi,calc}$) from the training catchments irrespective of the catchment size. The average estimated specific DSi mobilization ($f_{DSi,mob}$) of the 140 training catchments considered here (2.57 t SiO_2 km^{-2} a^{-1}) is only 1.5 % lower than the average $f_{DSi,calc}$ (2.61 t SiO_2 km^{-2} a^{-1}). For the total DSi fluxes from the area covered by the training catchments, catchment size is indeed a factor, which is likely the cause for the higher discrepancy between total estimated DSi mobilization and total calculated DSi fluxes. As the relative difference between $f_{DSi,mob}$ and $f_{DSi,calc}$ per training catchment, expressed as DSi retention rate r_{DSi}, is not statistically related to catchment size (Fig. 4c), a general bias of DSi mobilization estimates related to catchment size can be excluded.

Mean air temperature is a potential factor of DSi mobilization, because mean air temperature has a positive effect on chemical weathering (e.g. Beusen et al. 2009; West et al. 2005; White et al. 1999). This factor was not included in the DSi mobilization equation, because it was not possible to isolate this factor as a statistically significant predictor (Jansen et al. 2010). The DSi mobilization estimates show a tendency to overestimate DSi mobilization in colder regions and underestimate DSi mobilization in warmer regions (Jansen et al. 2010; Moosdorf et al. 2011), which could be explained by a temperature dependence of chemical weathering. However, as the training catchments are on average only slightly colder than the whole monitored area (−0.6 °C) (Table 6), no notable bias in the estimated total DSi mobilization and thus DSi retention from this tendency is expected.

With regard to land cover, a weak tendency of underestimating DSi mobilization from agricultural lands and grasslands was identified (Jansen et al. 2010; Moosdorf et al. 2011). In this study, this tendency is confirmed by a low negative correlation of DSi retention (r_{DSi}) to agricultural lands ($r = -0.22$) and grasslands ($r = -0.28$) within the training catchments, for which minimum retention effects are expected. However, as there is a strong positive intercorrelation between areal proportions of both land cover classes ($r = 0.67$, Table 8), it remains difficult to distinguish between the effects of both land cover classes. An increased DSi mobilization from cultivated land due to the depletion of the soil BSi pools was reported by recent studies (Clymans et al. 2011; Struyf et al. 2010a). These effects are a possible explanation for the underestimation of DSi yields from agricultural lands by the DSi mobilization model that only refers to chemical rock weathering as source of fluvial DSi (Jansen et al. 2010). However, as average land cover composition of the training catchments and the monitored area is similar (Table 7), it is not

Table 8 Correlation matrix[a] of catchment parameters, refers to set of all 624 catchments considered in this study

	Catchment size	Log_{10}(Catchment size)	Mean air temp. ($T_{air,mean}$)	Acricultural land (A_{AL})	Broad-leaved forest (A_{BF})	Coniferous forest (A_{CF})	Shrub-land (A_{SL})	Grass-land (A_{HV})	Artificial areas (A_{AA})	Lake area proportion	Runoff (q)	Avg. DSi conc.	$f_{DSi,calc}$	$f_{DSi,mob}$	r_{DSi}
Catchment size	*1.00*	**0.44**	*−0.08*	*0.06*	*−0.06*	**−0.09**	**0.13**	**0.08**	*−0.05*	**0.16**	**−0.15**	*−0.02*	**−0.13**	**−0.10**	*0.02*
Log_{10}(Catchment size)		*1.00*	**−0.09**	**0.10**	**−0.10**	**−0.15**	**0.30**	**0.12**	**−0.22**	**0.21**	**−0.36**	**0.13**	**−0.25**	**−0.26**	*−0.07*
Mean air temp. ($T_{air,mean}$)			*1.00*	**0.11**	**0.19**	**−0.25**	**−0.21**	**0.17**	**0.16**	**−0.14**	*−0.01*	**−0.13**	*−0.06*	*−0.03*	**0.15**
Acricultural land (A_{AL})				*1.00*	**−0.39**	**−0.57**	**−0.14**	**0.67**	**−0.11**	**−0.10**	**−0.33**	*0.06*	**−0.26**	**−0.24**	*0.01*
Broadleaved forest (A_{BF})					*1.00*	**−0.38**	**−0.30**	**−0.25**	**−0.14**	*−0.03*	**0.24**	**−0.34**	*−0.06*	*0.01*	**0.19**
Coniferous forest (A_{CF})						*1.00*	0.03	**−0.60**	**0.08**	*0.07*	**0.36**	**0.12**	**0.50**	**0.41**	**−0.14**
Shrubland (A_{SL})							*1.00*	**−0.19**	−0.07	*−0.06*	**−0.38**	**0.34**	**−0.20**	**−0.24**	**−0.15**
Grassland (A_{HV})								*1.00*	*−0.03*	**−0.12**	**−0.41**	*0.07*	**−0.35**	**−0.32**	*0.01*
Artificial area (A_{AA})									*1.00*	*−0.02*	*0.04*	*−0.08*	*0.00*	*0.04*	**0.09**
Lake area proportion										*1.00*	*0.02*	*−0.08*	*0.00*	*0.01*	*0.04*
Runoff (q)											*1.00*	**−0.30**	**0.75**	**0.75**	*0.06*
Avg. DSi conc.												*1.00*	**0.14**	*−0.08*	**−0.68**
$f_{DSi,calc}$													*1.00*	**0.83**	**−0.27**
$f_{DSi,mob}$														*1.00*	**0.08**
r_{DSi}															*1.00*

[a] Correlations which are significant to the $p = 0.05$-level are highlighted in bold, non-significant correlations are in *italic*

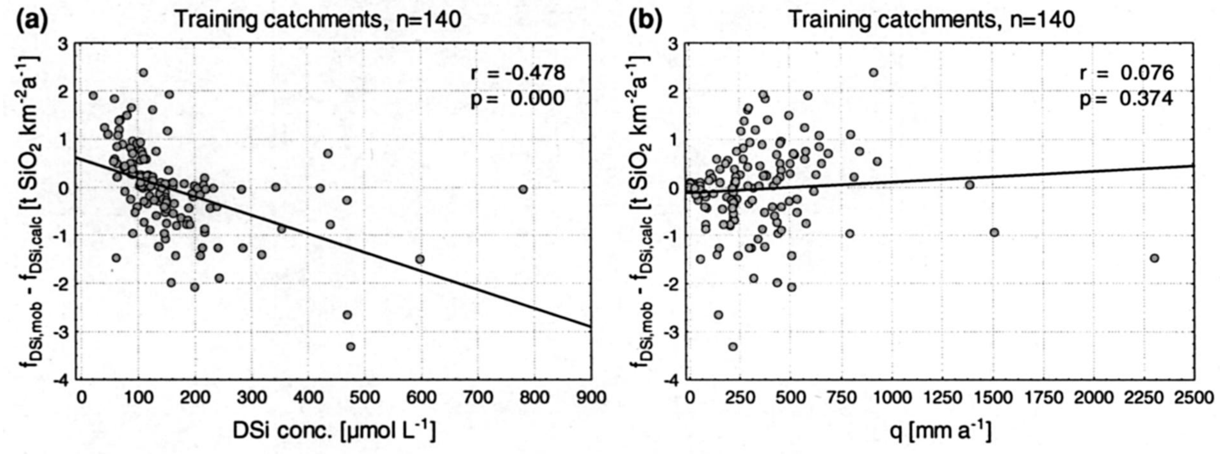


Fig. 5 Difference between estimated mobilization and calculated DSi fluxes versus **a** DSi concentrations derived from hydrochemical monitoring data and **b** the runoff data used for flux calculations—both within the training catchments

expected that the total DSi mobilization estimated for the study area and the thereupon derived estimate of total DSi retention is biased by land cover effects.

Generally, the estimates of DSi mobilization tend to overestimate specific fluxes with low DSi concentration and to underestimate specific DSi fluxes with high DSi concentrations within the training catchments (Fig. 5a). Albeit, there is no significant correlation between under- and overestimation of specific DSi fluxes and runoff (Fig. 5b). The regional clustering of negative DSi retention rates corresponds with the regional clustering of rivers with high average DSi concentrations (Figs. 2, 3). Particularly for tributary areas of the West Coast (San Francisco Coast and South Cascadia Basin, Table 3), the spatially explicit estimates of DSi mobilization had even to be increased to represent a regionalized estimate of fluvial DSi exports.

Additional sources of DSi

Two potential sources of DSi are neglected in this study: atmospheric inputs and anthropogenic point sources. Atmospheric depositions of silica onto the water surface is usually negligible in the silica budget of freshwater ecosystems (e.g. Hofmann et al. 2002; Ladouche et al. 2001). In the Great Lakes, where lake area is extensive compared to the contributing terrestrial area and, thus, fluvial inputs of DSi, atmospheric inputs are more likely of significance than in other river catchments with lower lake area proportions. However, the ratio of fluvial silica imports (DSi + BSi) to atmospheric depositions is 16:1 for Lake Superior (Johnson and Eisenreich 1979) and more than 25:1 for Lake Michigan (Parker et al. 1977). Thus, it is concluded that direct atmospheric inputs to the fluvial systems are generally negligible within the study area.

For Europe, the contribution by anthropogenic point sources to fluvial silica fluxes was estimated to be 2 % on average (van Dokkum et al. 2004). Within the Seine River basin, anthropogenic silica is estimated to make up as much as 8 % of total inputs in dry years, when terrestrial ecosystems as diffuse sources contribute less (Sferratore et al. 2006). The average domestic contribution according to the budget by Sferratore et al. (2006) is about 781 g SiO_2 a^{-1} $inhabitant^{-1}$ and stems mainly from food and detergents. Anthropogenic point sources, i.e. waste water treatment plants, were also shown to be a significant DSi source in the Hudson River estuary (Clark et al. 1992) in the north eastern part of our study area. Besides waste water effluents, urban areas can further be places of increased DSi exports due to inhibited plant uptake of DSi on impervious surfaces or highly compacted soils (Carey and Fulweiler 2011).

Anthropogenic point sources were avoided for the DSi mobilization estimation by using rather pristine training catchments (Jansen et al. 2010). The 140 training catchments considered here have an average population density of 9.2 inhabitants per km^2. Taking the values given by Sferratore et al. (2006) as first-order approximation, an average anthropogenic contribution of 7.2 kg DSi per km^{-2} a^{-1} from domestic sources would result, i.e. less than 0.3 % of the average estimated DSi mobilization of 2.57 t SiO_2 km^{-2} a^{-1}. The total monitored area considered here has an average population density of 26.5 inhabitants per km^2. Adding this domestic silica, the DSi mobilization within the monitored area could be estimated to be 1.3 % higher, and the estimated total retention would increase from 13 to 14 %. However, as Sferratore et al. (2006) state, these assumptions on domestic DSi inputs cannot be easily transferred.

Although silica inputs from point sources are minor compared to natural diffuse inputs from the terrestrial system, industrial inputs, especially from pulp and paper mills, can be substantial (van Dokkum et al. 2004). However, at a regional scale, no appropriate data set on industrial sources is available. Despite being in general a minor source of DSi, anthropogenic sources contribute to the uncertainties in the estimation of DSi retention in some areas.

Limitations due to scarce BSi data

A major problem of the budget calculations presented here is the scarcity of data on BSi concentrations, as DSi is transformed to BSi by biotic uptake and a major part of BSi is redissolved to DSi within aquatic ecosystems.

The approach to calculate silica retention based on DSi alone requires the assumption that the concentrations of BSi relative to DSi are negligible or, at least, that BSi concentrations relative to DSi concentrations would be similar for different catchment sizes. However, according to the data compiled by Conley (1997), BSi contributes about 16 % of the global fluvial silica export. The data further suggest that in small catchments BSi/DSi ratios tend to be lower than in larger catchments. This could cause the approach presented here to overestimate silica retention.

On the other hand, other studies show that small impoundments with very short residence times act mainly as a trap for riverine diatoms and decrease BSi concentrations downstream whereas DSi concentrations upstream and downstream of the impoundments can be quite similar (Humborg et al. 2006; Triplett et al. 2008). In these cases, retention of silica can be significant but would not be detected by a budget based on DSi concentrations alone.

The proportions of BSi fluctuate seasonally due to diatom growth, with about 50–70 % during diatom blooms and 10–20 % throughout the rest of the year (Conley 1997). Besides the general seasonal patterns, abundance of diatom BSi in the water can fluctuate significantly on even shorter timescales responding to short-term changes in nutrient concentration and light conditions, substantially adding to the uncertainty related to sampling frequency and flux estimation (cf. Triplett et al. 2008).

Furthermore, soil erosion can be a substantial source of terrestrial BSi, mainly consisting of plant phytoliths (e.g. Cary et al. 2005; Smis et al. 2010). The dissolution of such terrestrial BSi is considered a potential source of DSi within the fluvial system (e.g. Triplett et al. 2008). However, to the authors no study quantifying such a contribution is known. The in-river dissolution of terrestrial BSi could be a possible explanation for the underestimation of fluvial DSi fluxes from agricultural areas and grasslands, as these are accumulating large amounts of phytoliths and/or can be susceptible to soil erosion (e.g. Conley 2002).

Assumption of steady state

Additional uncertainties in the approach presented here are due to the assumption of a steady state for the DSi mobilization from the terrestrial system as well as for DSi retention within freshwater systems. For their empirical DSi mobilization equation, Jansen et al. (2010) identified runoff and lithology as major predictors. Thus, the empirical equation suggests that DSi liberation by chemical rock weathering directly determines the DSi mobilization into rivers. Indeed, it was shown that in most ecosystems substantial plant and soil storages of amorphous silica exist and cycling of silica between these storages is likely to be in the order of magnitude of DSi exports and often exceeds them (Conley 2002; Fraysse et al. 2010; Borrelli et al. 2010; Alexandre et al. 1997; Blecker et al. 2006; Fulweiler and Nixon 2005; Struyf et al. 2010a; Street-Perrott and Barker 2008; Cornelis et al. 2010). Thus, tracing DSi fluxes in rivers back to weathering presupposes that the terrestrial ecosystems are in a steady state with no net changes in BSi storages. However, disturbances in terrestrial ecosystems, likely due to anthropogenic perturbation, may lead to changes in terrestrial silica storages, and thus may influence the rate of DSi exports to rivers (Carey and Fulweiler 2011; Clymans et al. 2011; Conley et al. 2008; Melzer et al. 2010; Struyf et al. 2010b). Such effects may have biased the empirical mobilization equation by Jansen et al. (2010) and could be a reason for the tendency to underestimate DSi mobilization from agricultural lands and grasslands. In order to assess such impacts, more research and data on soil and plant BSi pools as well as detailed information on recent land cover changes are needed.

Calculating estimates of DSi retention in the approach presented here also assumes steady state conditions in freshwater ecosystems with constant annual rates of biotic DSi uptake and net-losses of BSi to sediments. However, the variability and complexity of environmental controlling factors causes interannual variations in diatom growth and thus DSi retention that are difficult to predict (e.g. Ferris and Lehman 2007; Koch et al. 2004). Furthermore, the ecological status of a freshwater ecosystem may be in transition due to changes in its trophic level (c.f. Conley et al. 1993; Hartmann et al. 2011) and alterations in hydrology due to dams and locks (c.f. Humborg et al. 2006). For such a transition due to eutrophication, Schelske (1985) gives an example for the Great Lakes which was characterized by a negative mass balance with silica outflows exceeding silica inflows. This transition has led from a steady state with N and P limiting diatom growth to a new steady state with DSi limitation and was characterized by a lasting depletion in DSi storages within the water column. Such a transition is a possible reason for negative mass balances for distinct reservoirs reported by Kelly (2001) (Table 5). However, longer time series of inflows and outflows of DSi and BSi to/from lakes and reservoirs as well as in-reservoir/in-lake silica cycling would be needed to confirm such a hypothesis, at present not available for a continental-scale data base.

Conclusion

This study investigated the possibility to assess the retention of dissolved silica (DSi) in the fluvial system of the conterminous USA based on a spatially explicit estimate of DSi mobilization into streams and rivers and fluvial DSi fluxes calculated from hydrochemical monitoring data. Uncertainties of DSi retention estimates, which arise from uncertainties related to the DSi mobilization estimates and the calculation of DSi fluxes, are large compared to expected DSi retention rates. Thus, the approach presented here does not allow deriving certain DSi retention rates for individual rivers catchments, nor does it allow the identification of functional relations between DSi retention and potential controlling factors. However, comparison to literature values suggests that the DSi retention rates estimated in this study are reasonable for the St. Lawrence River Basin ($r_{DSi} = 91$ %), which comprises the Great Lakes and is thus characterized by very high water residence times, and for the Mississippi River Basin (at Vicksburg, MS) ($r_{DSi} = 13$ %), which is the largest of the catchments considered (6.6 10^6 km^2, 44 % of the monitored area). For the whole study area, a DSi retention rate of 13 % relative to the estimated DSi mobilization was derived. This value is rather low compared to previous first order estimates and likely underestimates the total DSi retention due to an underestimation of DSi mobilization.

To improve our understanding of the land–ocean silica transfer, more elaborate models of DSi mobilization into streams and rivers are needed, which represent silica pools and cycling in terrestrial ecosystems. Further, more field studies on BSi concentrations and DSi–BSi transformation in the fluvial system, particularly within riverine lakes and reservoirs, are needed, which could provide an empirical basis for large scale estimates of silica retention and fluvial transport of total silica (DSi + BSi).

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