

# Changes in dissolved silicate loads to the Baltic Sea — The effects of lakes and reservoirs

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Received 22 August 2006; accepted 12 October 2007

Available online 23 December 2007

## Abstract

We tested the hypothesis that dissolved silicate (DSi) yields [ $\text{kg km}^{-2} \text{yr}^{-1}$ ] of 82 major watersheds of the Baltic Sea can be expressed as a function of the hydraulic load (HL) as a measure of water residence time and the total organic carbon (TOC) concentration, both variables potentially increasing the DSi yield. Most boreal rivers fitted a linear regression model using HL as an independent variable to explain the DSi yield. Rivers with high HL, *i.e.*, shortest residence times, showed highest DSi yields up to  $2300 \text{ kg km}^{-2} \text{yr}^{-1}$ . This is most likely caused by an excess supply of DSi, *i.e.*, the geochemical sources prevail over biological sinks in these boreal watersheds. The DSi yield for regulated and unregulated larger rivers of the boreal watersheds constituting about 40% of the total water discharge and of the total DSi load to the Baltic Sea, respectively, can be expressed as:  $\text{DSi yield} = 190 + 49.5 \text{ HL} [\text{m yr}^{-1}] + 0.346 \text{ TOC } [\mu\text{M}]$  ( $R^2 = 0.80$ ). Since both HL and TOC concentrations have decreased after damming, the DSi yields have decreased significantly in the regulated boreal watersheds, for the River Luleälven we estimated more than 30%. The larger eutrophic watersheds draining cultivated landscape of the southern catchment of the Baltic Sea and representing about 50% of the annual water discharge to the Baltic Sea, deviated from this pattern and showed lower DSi yields between  $60\text{--}580 \text{ kg km}^{-2} \text{yr}^{-1}$ . DSi yields showed saturation curve like relationship to HL and it appears that DSi is retained in the watersheds efficiently through biogenic silica (BSi) production and subsequent sedimentation along the entire river network. The relationship between HL and DSi yields for all larger cultivated watersheds was best fitted by a Freundlich isotherm ( $\text{DSi} = 115.7 \text{ HL}^{109}$ ;  $R^2 = 0.73$ ), because once lake and reservoir area exceeds 10% of the watershed area, minimum DSi yields were reached. To estimate an unperturbed DSi yield for the larger eutrophic southeastern watersheds is still difficult, since no unperturbed watersheds for comparison were available. However, a rough estimate indicate that the DSi flux from the cultivated watersheds to the Baltic Sea is nowadays only half the unperturbed flux. Overall, the riverine DSi loads to the Baltic Sea might have dropped with 30–40% during the last century.

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**Keywords:** Dissolved silicate; Biogenic silica; Retention; River loads; Damming; Eutrophication; Baltic Sea

## 1. Introduction

On a global scale, dissolved silicate (DSi) river concentrations and loads have been described as a

function of runoff temperature and bedrock type (Meybeck, 1979) or runoff-temperature and physical denudation (Gaillardet *et al.*, 1999). These factors are also believed to be the major environmental variables controlling chemical weathering rates of silicate minerals. DSi yields range between roughly  $500\text{--}5000 \text{ kg km}^{-2} \text{yr}^{-1}$  globally and are highest in areas with high weathering

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rates, *i.e.*, in the Himalayans and watersheds on volcanic bedrocks (Jennerjahn et al., 2006). These authors stress also the significance of specific discharge that correlate significantly with DSi yields. On a regional scale, the global patterns between DSi yield and the above mentioned environmental variables are more difficult to observe, since the heterogeneity in landscape and hydrological variables between watersheds become clearly discernable in small to mid sized watersheds ( $10^2$  to  $10^5$  km<sup>2</sup>) compared to major global watersheds integrating various landcover types (Smith et al., 2005). For the same reasons, human impacts vary more between smaller watershed systems making it difficult to disentangle natural from anthropogenic effects on DSi land sea fluxes.

The effects of lakes in lowering DSi concentrations of aquatic systems and DSi loads to the sea has been first described by Schelske and Stoermer (1971) for the eutrophic Lower Great Lakes and by Van Bennekom and Salomons (1979) for the Aswan Dam and has been called the “artificial lake effect”. Dams convert a river into a lake, increasing water residence times and often improving light conditions in the water column giving the preconditions for algal growth, including diatoms. Diatoms frustules consists of biogenic silica (BSi) that is sequestered in the sediments; this effect is later on referred to as “particle trapping”. BSi trapping can be very efficient even in natural lakes. Hofmann et al. (2002) observed some 85% of the main Si export from Lake Lugano occurred via deposition and burial of diatom frustules in the sediments, and only less than 20% of the sediment loss was re-supplied to the water column by diffusion. Conley et al. (2000) have shown that lake area of a watershed and DSi concentrations are negatively correlated for Scandinavian rivers including eutrophic, but also ultraoligotrophic river systems. Thus, diatom blooms behind dams and subsequent sequestration of BSi in the reservoirs sediments (Conley et al., 1993) cannot be the only reason for the observed decrease in DSi concentrations. Later, it has been suggested that perturbed surface water–groundwater interactions through hydrological alterations leading to less contact of river and stream waters with vegetated soils along the riparian zone are additional causes for the reduced DSi concentrations observed in many ultraoligotrophic regulated rivers in Northern Sweden (Humborg et al., 2002; Humborg et al., 2006a); this effect is later on referred to as “weathering reductions induced by hydrological alterations”. Generally, there is accumulating evidence that plants play a significant role in the global Si cycle (Conley, 2002) and control even the riverine DSi export fluxes (Derry et al., 2005). DSi concentrations in the boreal rivers of Northern

Sweden can best be described as a function of vegetation and peatland cover (Humborg et al., 2004) as well as a function of the degree of damming (Humborg et al., 2002). For the eutrophic watersheds of the Baltic Sea the effect of BSi particle trapping has been demonstrated by comparing the moderately dammed Vistula with the undammed Odra and it has been concluded that a full trapping of diatom derived BSi might be responsible for some 25% reduction in DSi loads of these types of rivers (Humborg et al., 2006a). In heavily dammed eutrophic rivers possibly the co-occurrence of both effects, *i.e.*, weathering reductions induced by hydrological alterations and particle trapping, may lead to even lower DSi land–sea fluxes.

The aim of this paper is to investigate the effect of lentic waters (lakes and reservoirs) in different biomes of the Baltic Sea catchment and discuss probable past DSi inputs into the Baltic Sea; even effects of vegetation will be tested. The data set on DSi land–sea fluxes generated by the SIBER project covers the entire Baltic Sea catchments ( $1.73 \cdot 10^6$  km<sup>2</sup>), which include subarctic watersheds in the North, boreal watersheds along the major parts of Sweden, Finland and Russia and temperate watersheds in the southeastern part (Baltic States, Poland, Germany) and thus provides for the first time a full data set of DSi fluxes from all major rivers to the Baltic Sea. Previous data compilations can be found in the GLORI database that cover only a few rivers and is based on much less observations (Meybeck and Ragu, 1995). This new data base allows us for a first time to compare DSi fluxes in various biomes on this regional scale and to come up with a rough estimate on the possible reductions in DSi land–sea fluxes to the Baltic Sea due to anthropogenic impacts. This task is not straight forward, because a complete set of monitoring data on DSi river loads to the Baltic Sea exist since the 1980ies and show no significant trends (Papush and Danielsson, 2006), *i.e.*, the existing time series reflect the situation after major anthropogenic impacts as eutrophication and damming of rivers have already occurred. However there are other ways to estimate long-term trends in DSi. We will use the concept of water residence time that has been widely used to describe the riverine exports of nitrogen (N) and phosphorus (P), but to our knowledge not for DSi, to the coastal water bodies (Howarth, 1996; Nixon et al., 1996; Behrendt and Opitz, 1999), since lakes and reservoirs change the residence times significantly. We will test the hypothesis that effects of reservoirs and lakes will manifest differently in the different biomes of the Baltic Sea catchment, since the underlying processes, *i.e.*, weathering reductions induced by hydrological alterations and particle trapping, do play different roles in the various biomes.

## 2. Material and methods

### 2.1. Data sources

The analysed data set on watershed properties and river chemistry data comprised eighty-two watersheds. The investigated major river watersheds within the Baltic Sea catchment included all rivers having a mean water discharge  $>0.15 \text{ km}^3 \text{ yr}^{-1}$  and the area of the watersheds span from  $10^2$  to  $10^5 \text{ km}^2$  (Table 1). In total, these rivers comprised  $429 \text{ km}^3$  water discharge annually, which corresponds to more than 90% of all riverine water discharge into the Baltic Sea (Bergström et al., 2001).

The data used for land cover calculations were compiled from satellite images, with a spatial resolution of  $150 \times 150 \text{ m}$  (various reference data sets provided by the EU Joint Research Centre Ispra, Italy; <http://www-gvm.jrc.it/glc2000/>). Calculations of percentage land cover for each drainage area were performed using ARC VIEW® 8.1. The drainage basin boundaries were obtained from the Swedish Meteorological and Hydrological Institute (SMHI). Table 1 summarises land cover classes of the investigated watersheds.

Monthly observations of river nutrient data (Si, N and P) and hydrological data were taken from the Baltic Environmental Database (<http://www.mare.su.se/nest/>). These measurements represent river mouth data. These nutrient data were discharge weighted, and averaged using monthly data from 1980–2000.

### 2.2. Study area

The drainage basin of the Baltic Sea can be divided into a northern boreal part that drains into the Gulf of Bothnia (Bothnian Bay and Bothnian Sea) and a southern part that drains into the rest of the Baltic Sea. Land usage patterns vary significantly between the watersheds (Table 1). The northern watersheds are generally sparsely populated and less eutrophic (Humborg et al., 2003) compared with the cultivated and eutrophic watersheds of the south (Table 1). The dominating land cover in the north is boreal forest and wetlands. The watersheds of the south are dominated by cultivated areas and deciduous forest (Table 1).

### 2.3. Hydraulic load as a proxy for water residence time

Water residence time is one of most significant variables for the nutrient retention in lakes (Vollenweider and Kerekes, 1982), in rivers (Howarth et al., 1996; Behrendt and Opitz, 1999; Seitzinger et al., 2002) and

estuaries (Nixon et al., 1996). However, the estimate water residence time in watersheds and rivers is still a matter of discussion, since an accurate estimate requests information of evapotranspiration, groundwater vs. surface runoff fluxes and detailed information of depth and width of lakes and river stretches. A complete set of these variables were not available for all 82 watersheds. To make an approximation of the water residence time we used the concept of hydraulic load to estimate whether water passes a given watershed relatively fast or slow. The mean hydraulic load was calculated by the following equation:

$$HL = \frac{q[l \cdot \text{km}^{-2}\text{s}^{-1}] \cdot 8.64 \cdot 0.365}{W[\%]} [\text{m yr}^{-1}] \quad (1)$$

where  $q$  represents the specific runoff [ $1 \text{ km}^{-2} \text{ s}^{-1}$ ], and  $W$  the catchment water area in percent. The hydraulic load gives the average annual value of the height of the water column flowing over  $1 \text{ m}^2$  water surface of a river system (Behrendt and Opitz, 1999). Note, that a significant amount of rivers draining into the Baltic Sea have been used to elaborate this empirical relationship.

### 2.4. Statistical analysis

Regression analyses were used to analyse the relationship between nutrient yields and watershed properties using MINITAB version 14.2. We analysed both the entire dataset of major Baltic Sea rivers ( $n=82$ ) and in addition the “larger” watersheds ( $>10^5 \text{ km}^2$ ;  $n=28$ ) within this group; this appears motivated, since the heterogeneity in landscape and hydrological variables in the smaller Baltic Sea watersheds ( $<10^5 \text{ km}^2$ ) are not representative for the major part of the river water fluxes. In fact, the larger rivers constitute only a third of the investigated rivers, but stand for some  $390 \text{ km}^3$  water discharge, which corresponds to more than 85% of all riverine water discharge into the Baltic Sea. To analyse the DSi patterns in unperturbed watersheds we even used data from smaller rivers, since there are only five rivers left in the Bltic Sea catchment that can be described as relatively unperturbed (Nilsson et al., 2005).

## 3. Results

### 3.1. DSi river concentrations

Fig. 1 shows the discharge weighted DSi concentration of 82 major rivers of the Baltic Sea catchment.

Table 1

Baltic Sea basins (BB=Bothnian Bay, BS=Bothnian Sea, BP=Baltic Proper, GF=Gulf of Finland, GoR=Gulf of Riga, KA=Kattegat), watersheds area, land cover discharge and specific runoff (Q), hydraulic load (HL), discharge weighted mean concentrations of total nitrogen (TN), total phosphorus (TP), total organic carbon (TOC), dissolved silicate (DSi), DSi load and DSi yield of 82 major rivers draining into the Baltic Sea; rivers commented on have been used in the regression analyses given in Fig. 4A and B

River	Basin	Comment	Area km <sup>2</sup>	Forest %	Wet-land %	Cult-vated %	Bare %	Water %	Discharge km <sup>3</sup>	Q 1 km <sup>-2</sup> s <sup>-1</sup>	HL m yr <sup>-1</sup>	TN μM	TP μM	TOC μM	DSi μM	DSi tons yr <sup>-1</sup>	DSi yield kg km <sup>-2</sup> yr <sup>-1</sup>
Töre älv	BB		406	96.8	1.1	0.7	0.0	1.4	0.1	11.4	25.4	37.7	1.1	1033	109.7	447	1102
Alterälven	BB		476	91.1	2.6	4.1	0.0	2.2	0.2	10.9	15.5	38.8	0.9	1066	120.4	549	1154
Kuivajoki	BB		1316	92.3	1.7	3.7	0.0	2.2	0.6	14.0	19.6	49.2	1.2	1493	103.7	1686	1281
Lestijoki	BB		1398	79.2	0.0	15.3	0.0	5.5	0.4	9.0	5.2	79.3	3.2	1820	113.7	1269	908
Rickleån	BB		1860	92.1	0.2	0.9	0.0	6.9	0.5	9.2	4.2	36.4	0.7	921	96.9	1465	788
Ähtävänjoki	BB		2014	73.6	0.5	16.4	0.0	9.4	0.5	8.0	2.7	59.7	1.4	1248	64.6	923	458
Perhonjoki	BB		2655	82.9	0.1	15.0	0.0	1.8	0.7	8.7	14.9	75.9	2.6	1760	109.5	2236	842
Simojoki	BB	unperturbed boreal	3218	87.9	3.0	3.1	0.0	6.0	1.4	13.3	7.0	37.7	0.9	1091	76.4	2892	899
Pyhäjoki	BB		3743	83.0	1.0	10.9	0.0	5.0	1.1	8.9	5.6	70.6	2.0	1553	106.0	3133	837
Kiiminkijoki	BB	unperturbed boreal	3755	94.8	0.8	1.5	0.0	3.0	1.4	12.0	12.6	41.0	1.2	1241	119.2	4755	1266
Lapuanjoki	BB		4133	73.3	0.5	24.1	0.0	2.1	1.1	8.8	13.1	126.7	3.0	1572	157.4	5053	1223
Räne älv	BB	unperturbed boreal	4137	78.1	18.5	0.9	0.0	2.6	1.3	10.0	12.1	27.0	0.6	667	109.0	3974	961
Kalajoki	BB		4158	80.1	0.2	18.2	0.0	1.2	1.1	8.2	21.5	108.4	3.7	2145	146.4	4423	1064
Siikajoki	BB		4372	81.2	1.6	15.2	0.0	2.0	1.4	9.9	15.3	68.1	2.5	1613	141.2	5419	1239
Kyrönjoki	BB		4844	71.3	0.9	26.9	0.0	0.8	1.4	9.2	36.2	160.9	3.4	1610	222.5	8768	1810
Pite älv	BB	regulated boreal	11209	74.3	15.2	0.3	5.0	4.9	5.8	16.3	10.5	18.8	0.5	342	66.0	10640	949
Skellefte älv	BB	regulated boreal	11577	75.6	7.0	0.6	4.6	12.0	5.3	14.6	3.9	18.5	0.3	358	43.2	6467	559
Iijoki	BB	regulated boreal	14264	92.4	0.9	1.7	0.0	5.1	5.5	12.3	7.7	29.2	0.8	889	101.2	15673	1099
Kalixälv	BB	unperturbed boreal	17674	72.1	20.3	1.2	3.5	2.5	10.0	17.9	22.3	25.6	0.8	480	80.0	22286	1261
Oulujoki	BB	regulated boreal	22825	86.3	0.7	1.8	0.0	11.1	8.5	11.8	3.4	26.8	0.7	757	45.8	10902	478
Lule älv	BB	regulated boreal	24934	62.4	14.6	0.9	13.3	7.4	16.7	21.3	9.0	14.5	0.3	229	42.2	19780	793
Torne älv	BB	unperturbed boreal	39613	73.2	18.0	1.2	2.6	4.8	13.5	10.8	7.2	26.5	0.9	589	86.4	32630	824
Kemijoki	BB	regulated boreal	50918	83.6	9.2	3.3	0.0	3.9	18.5	11.5	9.4	26.5	0.7	707	106.9	55486	1090
Median BB														<b>106.0</b>		<b>961</b>	
Forsmarksån	BS		410	91.1	0.0	5.7	0.0	3.2	0.1	6.7	6.5	74.0	0.8	1684	92.0	224	546
Sirppujoki	BS		468	83.5	0.0	15.9	0.0	0.6	0.1	8.1	42.7	197.0	2.7	nv	138.1	464	992
Laihianjoki	BS		471	73.8	0.0	26.0	0.0	0.2	0.1	7.7	114.6	198.1	2.6	nv	187.0	600	1273
Uskelanjoki	BS		819	58.2	0.1	39.9	0.0	0.4	0.2	7.2	57.2	195.4	7.7	1028	228.0	1186	1448
Aurajoki	BS		893	67.9	0.2	28.3	0.0	0.4	0.3	9.1	77.6	187.2	6.9	1216	202.6	1459	1634
Närpiönjoki	BS		970	80.3	0.3	18.7	0.0	0.7	0.3	9.7	44.4	147.0	2.5	1691	266.5	2216	2285
Kiskonjoki	BS		1101	79.6	0.3	17.1	0.0	3.1	0.3	7.3	7.5	83.2	1.9	931	104.4	746	677
Merikarvianjoki	BS		1105	92.5	0.1	1.2	0.0	6.2	0.6	15.9	8.1	67.7	1.4	1368	128.5	1992	1802
Isojoki	BS		1136	90.3	0.5	8.9	0.0	0.2	0.4	12.3	184.9	77.1	2.4	1518	194.5	2392	2105
Paimionjoki	BS		1145	56.5	0.2	41.7	0.0	1.2	0.3	7.7	20.6	202.9	7.7	1180	195.0	1519	1326
Eurajoki	BS		1346	71.3	0.1	14.9	0.0	13.6	0.3	8.0	1.9	128.9	2.2	094	110.4	1052	781
Lögde älv	BS		1777	96.1	0.9	1.1	0.0	1.8	0.6	11.2	19.4	26.1	1.0	771	109.1	1910	1075
Delångersåir	BS		1975	86.9	0.0	1.8	0.0	10.2	0.6	9.5	2.9	30.0	0.4	517	72.1	1191	603
Gavleån	BS		2279	84.7	0.2	4.2	0.0	7.1	0.7	9.6	4.3	58.8	1.0	993	66.2	1277	560
Karvianjoki	BS		2932	90.9	1.1	4.9	0.0	3.1	0.9	9.8	10.1	77.9	2.7	nv	77.1	1956	667
Öre älv	BS		2962	95.4	1.3	2.0	0.0	1.3	1.1	11.7	28.6	30.2	1.0	965	111.7	3428	1157
Gide älv	BS		3322	96.0	0.8	0.4	0.0	2.8	1.2	11.7	13.2	28.5	0.6	814	95.4	3267	983

Ljungan	BS	regulated boreal	13042	89.4	2.0	2.4	0.2	5.8	4.3	10.5	5.7	26.8	0.6	528	71.2	8605	660
Ljusnan	BS	regulated boreal	19751	89.2	4.3	2.5	0.0	3.7	7.5	12.1	10.3	29.8	0.5	577	90.8	19149	970
Indalsälven	BS	regulated boreal	25458	79.2	7.6	3.7	1.0	8.4	14.9	18.6	7.0	22.4	0.3	360	35.0	14614	574
Kokenmäenjoki	BS	regulated boreal	26667	78.7	0.3	10.1	0.0	10.2	8.1	9.6	3.0	85.5	1.9	909	67.1	15167	569
Ume älv	BS	regulated boreal	26737	82.5	6.7	1.3	3.7	5.6	14.8	17.6	9.8	17.4	0.4	360	49.8	20663	773
Dalälven	BS	regulated boreal	28873	86.1	3.4	4.8	0.0	5.1	11.9	13.1	8.2	31.6	0.6	600	70.3	23432	812
Angermanälven	BS	regulated boreal	31421	85.4	4.2	2.7	1.3	6.3	16.9	17.1	8.5	19.6	0.4	435	49.2	23316	742
Median BS															<b>99.9</b>		<b>891</b>
Ljungbyån	BP		689	86.1	0.0	11.7	0.0	0.1	0.1	6.2	134.9	121.9	1.2	1185	166.6	629	912
Lyckebyån	BP		830	93.2	0.0	3.8	0.0	1.5	0.2	7.2	15.2	69.2	0.9	1300	128.6	682	822
Botorpsströmmen	BP		1040	86.1	0.0	9.6	0.0	4.3	0.2	5.6	4.1	55.6	0.6	890	47.5	242	233
Kasari	BP		2950	48.7	0.4	50.8	0.0	0.1	0.9	9.4	292.0	283.6	1.6	nv	56.5	1386	470
Nyköpingsån	BP		3258	67.1	0.2	20.8	0.0	10.2	0.7	6.8	2.1	69.6	1.4	846	30.1	589	181
Mörrumsån	BP		3367	81.1	0.1	5.9	0.0	11.9	0.9	8.1	2.2	58.2	0.7	865	49.9	1210	359
Emån	BP		4559	87.1	0.0	9.0	0.0	3.1	0.5	3.4	3.4	67.2	0.7	1369	98.7	1339	294
Helge å	BP		4684	65.4	0.1	29.3	0.0	4.0	1.4	9.2	7.3	121.1	1.3	1202	114.7	4380	935
Venta	BP	eutrophic agricultural	11597	36.5	0.1	62.1	0.0	0.6	2.5	6.8	34.6	225.5	1.6	nv	81.0	5617	484
Pregolia	BP	eutrophic agricultural	14749	22.2	0.3	74.5	0.0	2.0	3.0	6.5	10.3	125.7	1.5	nv	78.8	6648	451
Motala ström	BP	eutrophic agricultural	15544	59.6	0.2	20.3	0.0	18.6	2.8	5.8	1.0	63.6	1.2	623	30.4	2414	155
Norrström	BP	eutrophic agricultural	22534	64.2	0.3	21.9	0.0	10.3	5.4	7.6	2.3	49.6	1.1	591	22.3	3363	149
Neman	BP	eutrophic agricultural	92104	36.8	0.4	61.0	0.0	1.0	16.3	5.6	17.6	247.0	2.7	nv	68.8	31423	341
Odra	BP	eutrophic agricultural	117589	32.6	0.6	64.2	0.0	0.8	16.9	4.5	19.1	312.5	12.1	nv	123.3	58257	495
Vistula	BP	eutrophic agricultural	192899	33.2	0.5	64.3	0.0	0.8	33.6	5.5	22.1	261.7	5.9	nv	118.8	111851	580
Median BP															<b>18.8</b>		<b>451</b>
Virojoki	GF		324	81.5	0.2	11.2	0.0	1.2	0.1	14.5	38.8	98.7	2.0	1134	128.9	535	1646
Keila	GF		565	43.9	0.0	55.0	0.0	0.3	0.2	12.1	143.5	332.5	1.8	nv	72.1	434	769
Mustionjoki	GF		814	78.0	0.1	20.1	0.0	1.2	0.6	25.3	64.5	68.6	1.2	626	44.7	812	997
Koskenylänjoki	GF		830	64.8	0.5	29.7	0.0	5.0	0.3	10.8	6.8	128.8	3.4	777	110.8	873	1052
Porvoonjoki	GF		1306	66.0	0.0	30.8	0.0	1.0	0.4	10.8	35.7	239.7	4.8	954	152.4	1897	1452
Vantaa	GF		1726	65.9	0.1	22.9	0.0	2.0	0.5	10.0	15.9	185.2	4.3	1071	162.3	2465	1428
Kymijoki	GF	regulated boreal	36522	77.8	0.2	2.6	0.0	19.0	9.9	8.6	1.4	41.0	0.7	672	36.9	10255	281
Narva	GF	eutrophic agricultural	56665	39.5	0.4	51.8	0.0	7.9	13.7	7.7	3.1	49.2	1.2	nv	51.0	19549	345
Neva	GF	eutrophic agricultural	285835	67.7	0.5	14.8	0.0	16.7	79.7	8.8	1.7	50.7	1.5	nv	8.0	17927	63
Median GF															<b>72.1</b>		<b>997</b>
Salaca	GR		3624	48.6	0.2	49.3	0.0	1.7	1.0	9.1	17.0	165.1	1.0	nv	73.4	2135	589
Päimu	GR		6173	52.1	0.4	46.6	0.0	0.3	1.7	8.9	103.8	175.9	1.8	nv	56.6	2747	445
Gauja	GR		8632	61.7	0.1	37.2	0.0	0.6	2.4	8.7	48.9	166.7	1.1	nv	89.5	5920	686
Lielupe	GR	eutrophic agricultural	17835	28.4	0.2	70.0	0.0	0.5	3.4	6.1	34.8	386.6	3.1	nv	70.1	6696	375
Daugava	GR	eutrophic agricultural	85853	45.8	0.5	51.4	0.0	1.7	21.1	7.8	14.2	132.7	2.0	nv	59.9	35321	411
Median GR															<b>70.1</b>		<b>445</b>
Rönneån	KA		1896	44.5	0.4	50.7	0.0	3.1	0.4	6.3	6.5	170.5	1.7	818	112.9	1184	625
Viskan	KA		2153	84.4	0.0	10.2	0.0	3.1	1.3	18.7	19.2	84.4	1.4	624	80.2	2851	1324
Nissan	KA		2738	90.8	0.3	5.0	0.0	2.5	1.3	15.4	19.4	65.3	0.9	1037	101.6	3787	1383
Ätran	KA		3364	83.0	0.0	12.5	0.0	3.8	1.4	12.8	10.7	83.5	0.7	736	82.0	3122	928
Lagan	KA		6353	82.4	0.6	8.2	0.0	8.1	2.4	12.0	4.7	62.7	0.7	876	71.2	4786	753
Göta älv	KA	eutrophic agricultural	48214	66.8	1.5	13.3	0.2	17.4	17.8	11.7	2.1	60.5	0.6	415	17.3	8586	178
Median KA															<b>81.1</b>		<b>841</b>

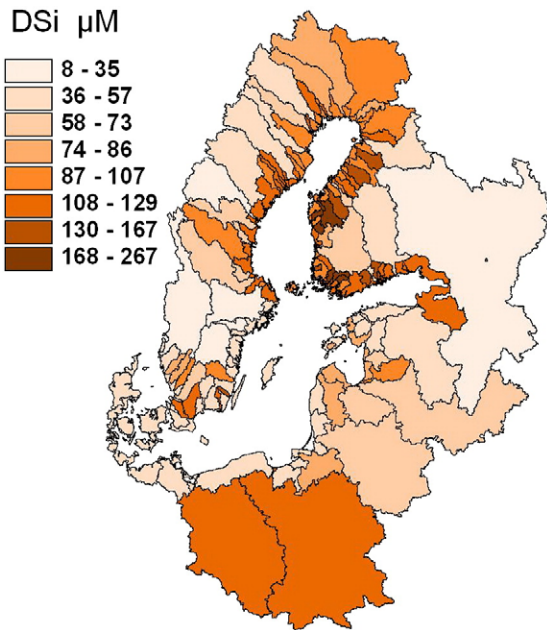


Fig. 1. Mean (1980–2000) discharge weighted dissolved silicate (DSi) concentrations of 82 major rivers draining into the Baltic Sea.

Highest DSi concentrations were found for the northernmost rivers, i.e., the rivers entering the Gulf of Bothnia have medians  $\sim 100 \mu\text{M}$ . Compared to these rivers, the rivers discharging into the Gulf of Finland, the Gulf of Riga, the Baltic Proper and the Kattegat all have medians between 70–80  $\mu\text{M}$ .

Minor rivers discharging into the Gulf of Bothnia and the northern part of the Gulf of Finland generally showed the highest DSi concentrations. This is especially true for some Finnish rivers located close to the sea, i.e., draining mostly lowlands with boreal forests and peatlands, (e.g. the Lestijoki, Kalijoki and Kyönjoki; Bothnian Bay and the Aurajoki, Paimianjoki and Sirppujoki; Bothnain Sea). These also showed elevated TN and TP concentrations and very high TOC concentrations  $> 1000 \mu\text{M}$  (Table 1).

Most of the major Swedish rivers running into the Bothnain Bay and Bothnian Sea are heavily regulated and have DSi concentrations between 40–60  $\mu\text{M}$ . The only exceptions are the northernmost rivers Kalixälven and Torneälven which can be described as almost unperturbed. The latter rivers showed significantly higher DSi concentrations of about 85  $\mu\text{M}$ .

Lowest DSi concentrations were seen in the major rivers Neva (8  $\mu\text{M}$ ), the Götaälv (17  $\mu\text{M}$ ), the Motalaström (30  $\mu\text{M}$ ) and the Norrström (22  $\mu\text{M}$ ). They are the effluents of the four largest lakes within the Baltic Sea catchment, the Ladoga in Russia and the Vänern, Vättern and Mälaren in Sweden.

The four major rivers Odra, Vistula, Daugava and Neman, all heavily eutrophic with elevated TN and TP concentrations, dominate the southeastern part of the Baltic Sea catchment (Table 1). However, whereas the watersheds of the Odra and Vistula consist of only small amounts of water areas, the watersheds of Daugava and Neman are heavily dammed or drain agricultural areas with high proportions of water areas. The DSi concentrations in the Odra (123  $\mu\text{M}$ ) and the Vistula (118  $\mu\text{M}$ ) were about double as high as the DSi concentrations in the Daugava (60  $\mu\text{M}$ ) and Neman (69  $\mu\text{M}$ ).

### 3.2. DSi yields vs. specific discharge and lake area

DSi yields [ $\text{kg km}^{-2} \text{yr}^{-1}$ ] of the 82 major Baltic Sea watersheds varied between 63 to 2,285  $\text{kg km}^{-2} \text{yr}^{-1}$  and

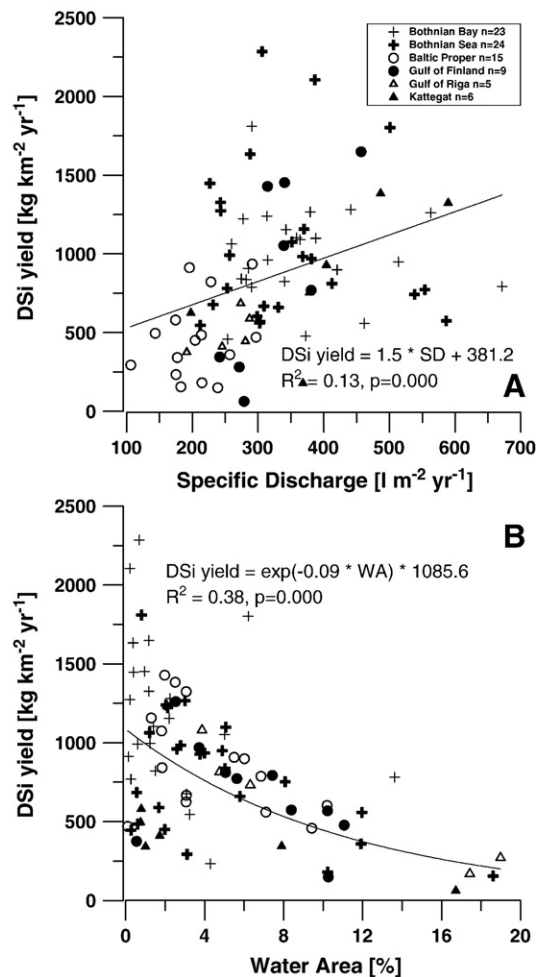


Fig. 2. Dissolved silicate (DSi) yield of 82 major watersheds draining into the Baltic Sea vs. (A) specific discharge (SD) and (B) watershed water area (WA).

are typical for arctic and temperate regions (Humborg et al., 2006b; Jennerjahn et al., 2006). Generally, the DSi yields were about double as high in the northern part of the catchment (Bothnian Bay, Bothnian Sea and Gulf of Finland) compared to the southern part (Baltic Proper, Gulf of Riga and Kattegat); Table 1). The regression analysis between specific discharge [ $\text{l m}^{-2} \text{yr}^{-1}$ ] and DSi yield showed only a slight positive correlation ( $R^2=0.13$ ,  $p=0.000$ ; Fig. 2A), but the variability is high. However, looking at the correlation coefficient basinwise the picture became clearer. The two northern most Baltic Sea basins, Bothnian Sea and Bothnian Bay and the Baltic Proper showed no correlation between DSi yield and specific discharge, while the correlation coefficients for the Kattegat ( $R^2=0.47$ ,  $p=0.128$ ) and the Gulf of Finland ( $R^2=0.54$ ,  $p=0.132$ ) and the Gulf of Riga ( $R^2=0.43$ ,  $p=0.222$ ) were higher. The Baltic

Proper was in between with a correlation coefficient of 0.30.

The DSi yield expressed as a function of water area (Fig. 2B) of all watershed gives a more significant result and was best fit by an exponential function ( $R^2=0.38$ ,  $p=0.000$ ). Also this relationship varied greatly between basins, where the relationship was insignificant for Gulf of Riga, moderate for Baltic Proper and Bothnian Sea ( $R^2>0.33$ ) and strong for the other three basins ( $R^2>0.66$ ).

### 3.3. DSi yields vs. hydraulic load

DSi yields of the major rivers draining the Baltic Sea catchment are shown in Fig. 3A and B as a function of the hydraulic load; watersheds were clustered by the concentrations of dissolved inorganic phosphorus (DIP, Fig. 3A) and dissolved inorganic nitrogen (DIN, Fig. 3B) concentrations. Apparently, the more oligotrophic rivers, *i.e.*, most of the rivers entering the Bothnian Bay and Bothnian Sea, showed a linear increase with the hydraulic load, whereas those rivers with higher concentrations of DIP and DIN, *i.e.*, those rivers draining the cultivated areas of the southern catchment, deviated from this linear pattern.

A linear relationship between hydraulic load and DSi yields (Fig. 4A) holds for both the larger regulated boreal rivers ( $4\text{--}17 \text{ km}^3 \text{ yr}^{-1}$  with a total discharge of  $143 \text{ km}^3 \text{ yr}^{-1}$ ;  $R^2=0.68$ ,  $p=0.000$ ) as well as for unperturbed boreal rivers ( $1.3\text{--}13 \text{ km}^3 \text{ yr}^{-1}$  with a total discharge of  $27 \text{ km}^3 \text{ yr}^{-1}$ ;  $R^2=0.65$ ,  $p=0.101$ ), whereas the regulated rivers form a group of rivers with lower hydraulic load, *i.e.*, longer residence time, and lower DSi yields compared to the unperturbed boreal rivers. A larger set of unperturbed rivers would have been desirable for a more sound statistical analysis, but only five major rivers (Kalixälven, Torneälven, Råneälven, Kiiminkijoki and Simojoki) can be regarded as unperturbed with respect to both nutrient concentrations (Table 1) and regulation *sensu* Nilsson et al. (2005).

A closer analysis focussing on the largest rivers of the southern part of the Baltic Sea catchment show that even for the eutrophic rivers, draining areas with considerable amounts of cultivated land, a significant relationship between hydraulic load and the DSi yield appeared, though not a linear one as for the boreal rivers (Fig. 4A). In this case the best fit ( $R^2=0.73$ ,  $p=0.000$ ) was achieved by using a Freundlich isotherm that is frequently used to describe adsorption/saturation processes and reaction rates. These rivers include besides others the Neva, Neman, Daugava, Vistula and Odra draining the south-eastern Baltic Sea catchment, but also the Götaälv, Motalaström and the Norrström in Sweden; in total this group represented together roughly 50% ( $216 \text{ km}^3$ ) of the

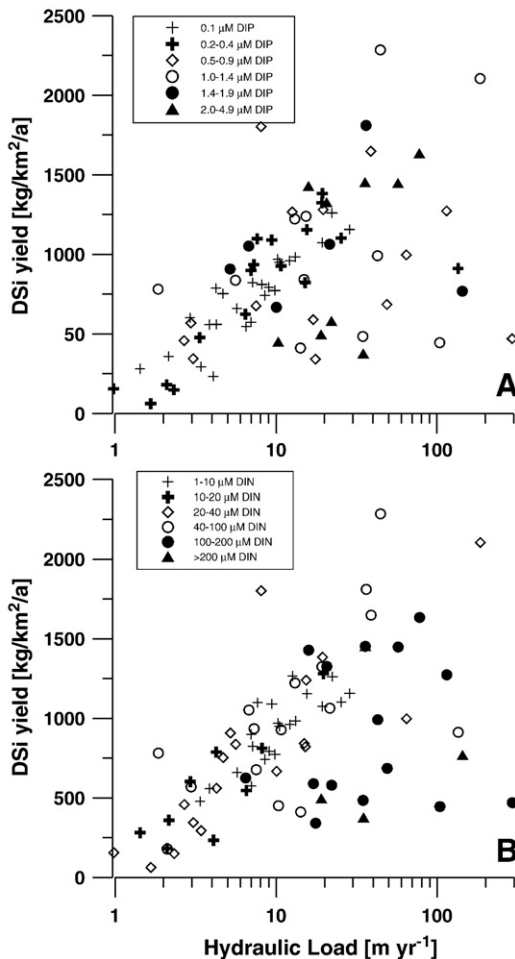


Fig. 3. Dissolved silicate (DSi) yield of 82 major watersheds draining into the Baltic Sea vs. hydraulic load; (A) grouped after dissolved inorganic phosphorus (DIP) concentrations and (B) grouped after dissolved inorganic nitrogen (DIN) concentrations.

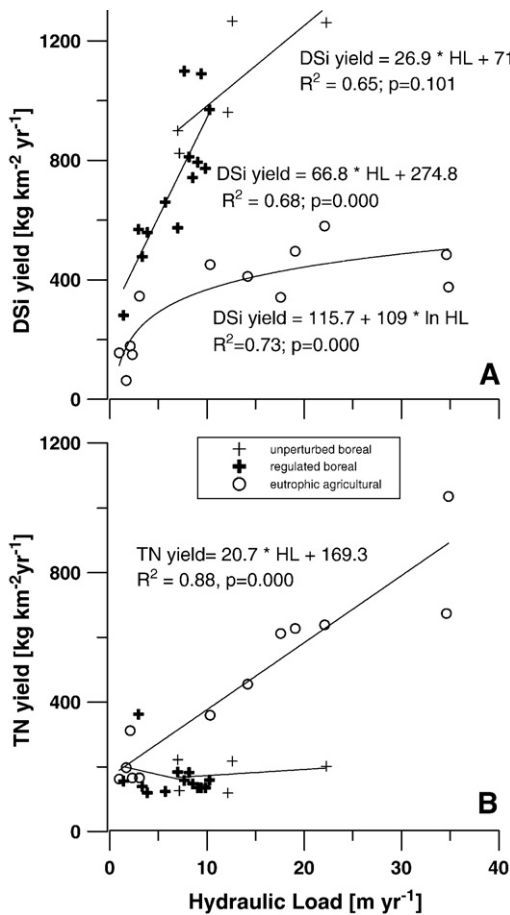


Fig. 4. (A) Dissolved silicate (DSi) yield of major watersheds ( $>10,000 \text{ km}^2$ ) draining into the Baltic Sea vs. hydraulic load (HL); (B) Total Nitrogen yields of major watersheds ( $>10,000 \text{ km}^2$ ) draining into the Baltic Sea vs. hydraulic load (HL).

annual riverine water discharge to the Baltic Sea. The rivers with the lowest hydraulic load ( $<5 \text{ m yr}^{-1}$ ) and DSi yields ( $<200 \text{ kg km}^{-2} \text{ yr}^{-1}$ ) were the Neva, the Götaälven, Norrström and Motalaström, *i.e.*, the effluents of the four largest lakes within the Baltic Sea catchment. These larger watersheds consisted of  $>10\%$  water cover and  $>13\%$  cultivated areas (Table 1). The remaining rivers of this group showed similar DSi yields disregarding the hydraulic load, thus, the DSi yields showed the saturation like relationship to the hydraulic load and even the Latvian Rivers, the Lielupe and the Venta with hydraulic loads  $>30 \text{ m yr}^{-1}$  showed comparable DSi yields with the nearby Estonian Rivers Narva that showed a hydraulic load of  $3.1 \text{ m yr}^{-1}$ . A comparable, but reverse picture appeared when plotting the total nitrogen (TN) yields of the same rivers as shown in Fig. 4A vs. the hydraulic load. Here, the cultivated watersheds showed a highly linear relationship with the hydraulic load ( $R^2=0.88, p=0.000$ ), whereas both the unperturbed and regulated boreal rivers

showed similar TN yields irrespective the hydraulic load (Fig. 4B).

### 3.4. Multiple regression analyses

The variability of landscape variables (Table 1) within the eutrophic watersheds of the southern catchment of the Baltic Sea, but also within the southern Swedish watersheds appeared to be too small and gave insignificant results when multiple variables were tested as significant environmental variables for DSi yields. Besides water residence times, vegetation cover has been shown to co-vary with high DSi concentrations in some watersheds of Northern Sweden (Humborg et al., 2004). Therefore we included TOC concentrations as a proxy variable for vegetation cover and tested its significance for DSi yields in the Northern part of the Baltic Sea catchment together with water residence time. DSi yield of the larger boreal watersheds (all unperturbed and regulated rivers draining into the Bothnian Bay and Bothnian Sea; see Fig. 4;  $n=19$ ) can be expressed as a function of the hydraulic load and the TOC concentration:

$$\text{DSi yield} = 190 + 49.5\text{HL} [\text{m yr}^{-1}] + 0.346\text{TOC} [\mu\text{M}] \quad (R^2 = 0.80; p = 0.000)$$

TOC values given in Table 1 are in average 74 times higher as HL for those rivers used in the regression analysis, but HL is by a factor 140 larger in the regression model, thus HL is about twice as significant as TOC for the observed DSi yield. Fig. 5 shows the expected DSi yields as calculated from the regression

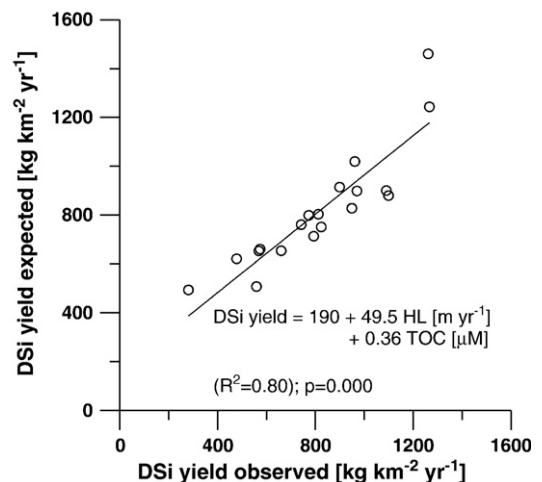


Fig. 5. Scatter diagram and regression equations for DSi yield ( $\text{kg km}^{-2} \text{ yr}^{-1}$ ), for 19 major boreal watersheds in the Baltic Sea catchment.

model plotted vs. the observed DSi yields showing the strong linear relationships holding over a wide DSi yield range from 200–1200 kg km<sup>-2</sup> yr<sup>-1</sup>.

#### 4. Discussion

The present study on DSi yields of major Baltic Sea watersheds suggest that both boreal and cultivated watersheds of the Baltic Sea catchment are heavily affected by hydrological alterations and eutrophication, the former leading to less weathering (Humborg et al., 2002), the latter leading to BSi trapping in lakes and reservoirs (Van Bennekom and Salomons, 1979; Conley et al., 1993; Humborg et al., 2000; Humborg et al., 2006a). Both these human impacts have decreased DSi yields significantly. As a consequence, distinct types of DSi yields occur in the perturbed watersheds of the Baltic Sea catchment when expressed as a function of water residence time or HL (Behrendt and Opitz, 1999). The regulated boreal watersheds showed lower DSi yields compared to the relatively unperturbed watersheds of the area and the DSi yields of both watershed types are linearly related to HL. The DSi yield of the cultivated watersheds of the southeastern catchment of the Baltic Sea followed a Freundlich isotherm (a saturation like relationship) when expressed as a function of HL. Opposite patterns occurred for the TN yields, *i.e.*, a linear relationship between TN and HL was obvious in cultivated watersheds, whereas the TN yield of the boreal watersheds was uniformly low irrespective whether the watersheds were regulated or relative unperturbed. A major implication from this study is that DSi is actively retained in the cultivated watersheds through diatom growth and sedimentation processes whereas in boreal watersheds DSi is still in excess and can be flushed out of the system. Since the two watershed types within the Baltic Sea catchment can be distinguished with respect to these DSi flux patterns, we will try in the following discussion to evaluate possible reductions in DSi land–sea fluxes to the Baltic Sea that have occurred during the last century.

##### 4.1. Boreal watersheds

DSi yields of the major watersheds within the Baltic Sea catchment are about twice as high in the northern boreal and subarctic part compared to the agriculture dominated and eutrophic southeastern part. In fact, DSi concentrations showed the opposite patterns to what is expected, since it is well known that chemical weathering rates of silicate minerals is related to temperature (Bernier and Bernier, 1995). The about 30% higher DSi concentration together with a higher specific discharge

explain these – for the Baltic Sea – relatively high DSi yields of the boreal catchment. They are in the same range of about 1 ton/km<sup>-2</sup> yr<sup>-1</sup> as observed in large Siberian and Canadian watersheds (Jennerjahn et al., 2006).

The DSi yield of many watersheds draining into the Gulf of Bothnia was most probably significantly higher before damming. It is obvious from Table 1 that the most regulated (*sensu* Nilsson et al., 2005) major rivers as the Luleälven, Skellefteälven, Ångermanälven, Oulijoki or Indalsälven showed much less DSi yields compared with the unregulated watersheds of which there are only five are left (Kalixälven, Torneälven, Råneälven, Kiiminkijoki and Simojoki) as reported by Nilsson et al. (2005).

Although changes in HL due to damming addresses hydrological changes in only parts of the major riverbed, its effect on DSi yield are significant. The concept of water residence time, here approximated by HL, and the TOC concentration as a further environmental variable significant for the DSi yield (Humborg et al., 2002; Millot et al., 2003; Humborg et al., 2004) are though of limited use to accurately estimate a decrease in DSi yields of the regulated rivers. First of all, historical data on TOC are not available before the 1970ies. Moreover, major reservoirs were mainly built in steep headwaters valleys and hence, a given increase in water area caused by a dam will represent only a minor fraction of the riverbed that has changed its hydrological settings. Between all reservoirs, the river flow is regulated either by headrace tunnels as in the case of most regulated rivers in Sweden (Jansson et al., 2000a,b) or by the balanced distribution of water discharges from the power plants, which reduces water level fluctuations in height (Carlsson and Sanner, 1994; Jansson et al., 2000a) along the river stretches of the entire system. Both prevent soil infiltration that is vital for the hyporheic exchange between river water and groundwater along the riparian zone. Hyporheic exchange has been found significant for Si weathering rates and Si supply to stream water in high latitude river systems (Gooseff et al., 2002; Maurice et al., 2002). Moreover the riparian zone of the major river beds contains the major part of weatherable alluvial deposits, whereas soil layers in these boreal catchments are generally thin. Thus, a quantitative measure for changes in hydrology along these segmented parts of the regulated rivers is needed to relate these changes to river biogeochemistry. The lake area in the Luleälven watershed for example has increased by at least 450 km<sup>2</sup> after regulation (Carlsson and Sanner, 1994), which corresponds to about 1.8% of the catchment area. A reduction of 1.8% in water area will increase the HL from 9 to 12 m yr<sup>-1</sup>

according to Eq. (1). This translates to a reduction in DSi yield between 150–200 DSi kg km<sup>-2</sup> yr<sup>-1</sup> by using the multiple linear regression equation describing DSi yields as a function of HL and TOC as well as the regression equation in Fig. 4A using only HL as a driving variable, respectively. Previous studies have shown that especially a high watershed cover with coniferous forest and peat are positive correlated to DSi concentrations whereas other factors as lithology were not shown to be significant for DSi fluxes on this regional scale (Conley et al., 2000; Humborg et al., 2004). Rivers draining watersheds with high cover in forest and peat also show high TOC concentrations (Table 1), *i.e.*, TOC can be regarded as a proxy of the latter landscape variables. The TOC concentration is much less in all heavily regulated rivers and can be explained by the almost entire destruction of the former riparian zone of the main river through unnatural flow regimes; a zone formerly rich in vegetation cover and wetlands (Carlsson and Sanner, 1994; Jansson et al., 2000a; Jansson et al., 2000b; Nilsson et al., 2005). If we further assume that the TOC concentrations in the Luleälven was about double as high before the hydrological alterations as it is today in the neighbouring and unperturbed river Kalixälven, then the decrease in DSi yield adds up to a further 100 kg km<sup>-2</sup> yr<sup>-1</sup> using the multivariate approach. Thus, this “fragmentary” estimate on DSi reductions suggests that the DSi yield of the River Luleälven has decreased by about 30%, which should be regarded as a minimum estimate.

Some of the Finnish rivers as for example the Kyrenjoki, Lapuanjoki, Paimianjoki and Uskelanjoki showed elevated DSi yields >1200 kg km<sup>-2</sup> yr<sup>-1</sup>, but were simultaneously rich in TN and TP with rather elevated concentrations between 100–200 μM and 3.0–7.0 μM, respectively; how is this possible? These watersheds are all small-scale lowland catchments dominated by boreal forest with low water cover, *i.e.*, rather few deposition sites for BSi. Moreover, these rivers showed very high TOC concentrations between 1000–1600 μM that consists mainly of colored DOM, *i.e.*, fulvic and humic acids, potentially causing light limitation along the lentic and lotic parts of these rivers (Benner, 2003).

#### 4.2. Cultivated watersheds

Obviously, the DSi yields of the large cultivated watersheds as the Neva, Götaälven, Odra, Vistula and Daugava deviate significantly from the much higher yields of the boreal watersheds. How much of these lower yields can be related to natural geomorphological

and hydrological settings and how much is due to human impacts is difficult to estimate, since there is simply no relatively unperturbed major watershed left as in the case for the boreal rivers. Different pressures affect both watersheds types, *i.e.*, the boreal watersheds are mostly influenced by hydrological alterations, whereas the cultivated watersheds are mainly affected by land use and eutrophication and to a minor extent by dam building, although also canalization of major parts of the river bed and flood control constructions along river banks might be of importance. However, we may roughly estimate that the unperturbed DSi yields of the cultivated watersheds might have been in the same range as the DSi yields of the unperturbed boreal watersheds, since the higher runoff temperature should have compensated for their lesser specific discharge. The weathering rate of silicate minerals increases by roughly 8% per one °C (Lasaga, 1998). The mean temperature within the major cultivated watersheds of the Vistula, Odra, Daugava and Neman is about 8 °C higher than in the unperturbed boreal watersheds with similar size (Kalixälven and Torneälven), which would result theoretically in a doubling of the weathering rate. On the other hand, the specific discharge of the Kalixälven and Torneälven is about double as high as in these major cultivated watersheds (Table 1), thus, the unperturbed DSi yields of both watershed types could have been about the same.

Within the group of the cultivated watersheds there are obvious patterns demonstrating the effect of biological retention. Lowest DSi yields (<200 kg km<sup>-2</sup> yr<sup>-1</sup>) were found in those watersheds with the highest amount of water area (>10%). The rivers Neva, Götaälven, Norrström and Motalaström drain the largest lakes of the Baltic Sea catchment namely the Ladoga, Vänern, Mälarena and Vättern, respectively that all are affected by eutrophication (Wilander and Persson, 2001; Willen, 2001; Rukhovets et al., 2003). However, these large lakes with a water residence times of years up to decades, were natural deposition sites for BSi as well in their unperturbed oligotrophic state. Thus, the DSi yields of these watersheds have probably been lower as the adjacent watersheds with less water area. A conceivable scenario could be that the DSi concentrations in these watersheds developed similarly to the DSi time series observed in the Great Lakes (Schelske and Stoermer, 1971; Conley et al., 1993) where roughly a reduction to one fourth of the pre-eutrophic DSi concentration, *i.e.*, from about 100 μM to 25 μM has been observed. In other words, the DSi yields of these watersheds were probably lower also in its pre-eutrophic state compared to watersheds with less water area and could have been in the order of 300–500 kg km<sup>-2</sup> yr<sup>-1</sup>.

The remaining major cultivated watersheds showed rather similar DSi yields (between 340–580 kg km<sup>-2</sup> yr<sup>-1</sup>) irrespective of the HL (Fig. 4A) compared to the much higher range observed in the boreal watersheds. Autochthonous production in these rivers can be significant, although the lake area of these watersheds is ≤2%. In the undammed Odra River, for example, BSi concentrations as high as 100 μM during the growth season were observed at the river mouth and the annual BSi load corresponded to about 30% of the DSi load (Humborg et al., 2006a). Total suspended sediment concentration of these rivers are generally low (<50 mg l<sup>-1</sup>; (Milliman et al., 1995) allowing for substantial diatom growth in these rivers. The BSi concentrations during summer when DSi is even depleted, only reach about half the DSi winter concentrations (Humborg et al., 2006a) suggesting additional deposition sites for BSi besides lakes and reservoirs as for example river banks, riparian wetlands, backwaters or polders distributed over the entire watershed. Recent studies from tidal wetlands for example have shown to contain and recycle large amount of BSi (Struyf et al., 2006; Struyf et al., 2007). This could explain the saturation like response of the DSi yield in relation to the HL and it appears that biological retention through diatom growth and subsequent sedimentation sets an upper limit of DSi yield in these watersheds between 500–600 kg km<sup>-2</sup> yr<sup>-1</sup>. The analogy with the boreal watersheds is striking, where TN yields are similar irrespective the water residence time since boreal forest is generally N limited (Dise and Wright, 1995; Vance and Chapin, 2001) and does not release N in substantial quantities. On the other hand, are both elements in excess due to either massive use of fertilizers in cultivated watersheds that can only partly be removed in the case of N (Boyer et al., 2002; Seitzinger et al., 2002) or through a constant supply via weathering and a practically absent diatom production in the case of DSi and boreal watershed (Karlsson et al., 2001; Humborg et al., 2002), they can be flushed out from the watershed.

## 5. Conclusion and outlook

Expressing the DSi fluxes in the Baltic Sea catchment as a function of hydraulic load resulted in obvious clusters of watershed types, where the unperturbed watershed showed highest fluxes followed by the regulated boreal watersheds and finally the cultivated watersheds. This indicates that the DSi land sea fluxes in the Baltic Sea area have decreased significantly, for the regulated boreal rivers with more than 30%, for the cultivated watersheds DSi fluxes may have halved. For the entire Baltic Sea this would indicate that the DSi

loads to the Gulf of Bothnia might have decreased with at least 120 000 tons DSi yr<sup>-1</sup>; the decrease in DSi loads to the Baltic Proper, Gulf of Riga and the Kattegat would sum up to additional 300 000 tons DSi yr<sup>-1</sup>. Overall, the riverine DSi loads to the Baltic Sea might have dropped with 30–40% during the last century.

Our study showed that two fundamentally different processes are responsible for the observed changes in DSi loads to the Baltic Sea. Both changes in weathering regime through hydrological alterations and diatom growth with subsequent trapping of BSi are still poorly understood and quantified. There is a continuous trend in decreasing DSi loads to many coastal areas with the potential to change the primary productivity regime of the coastal seas as has been observed for the Black Sea (Humborg et al., 1997) the Caribbean (Turner et al., 1998; Turner and Rabalais, 2003) and most recently in the China Sea (Chen et al., 2003). Future studies should not focus solely on large reservoir and dams, the DSi land–sea transport is affected along the entire river network. Studies on alterations in hyporheic exchange and weathering processes within the riparian zone as a consequence of hydrological alterations and BSi production and deposition patterns along all kinds of deposition sites within the entire river network are of vital importance for a more holistic approach to coastal biogeochemistry, from where Si has, unjustly, been left out for a long time.

## Acknowledgements

This research was a part of the project EU-project Silicate and Baltic Sea Ecosystem Response (SIBER, [www.siber.su.se](http://www.siber.su.se)). This work was financially supported by the European Commission (R&D Priority Sustainable Marine Ecosystems contract EVK3-CT-2002-00069) and in part by the Marine Research on Eutrophication Program ([www.mare.su.se](http://www.mare.su.se)). The following monitoring organisations have generously contributed to the river monitoring data: Finish Environmental Research Institute, Finland; Estonian Marine Institute, Estonia; Marine Monitoring Centre, Institute of Aquatic Ecology, Latvia; Lithuanian Maritime Safety Administration, Lithuania; Institute of Meteorology and Water Management, Poland; National Environmental Research Institute, Denmark; Department of Environmental Assessment, Uppsala Agricultural University, Sweden.

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