

Predicting riverine dissolved silica fluxes to coastal zones from a hyperactive region and analysis of their first-order controls

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Abstract Silicate weathering and resulting transport of dissolved matter influence the global carbon cycle in two ways. First by the uptake of atmospheric/soil CO₂ and second by providing the oceanic ecosystems via the fluvial systems with the nutrient dissolved silica (DSi). Previous work suggests that regions dominated by volcanics are hyperactive or even “hot spots” concerning DSi-mobilization. Here, we present a new approach for predicting DSi-fluxes to coastal zones, emphasizing “first-order” controlling factors (lithology, runoff, relief, land cover and temperature). This approach is applied to the Japanese Archipelago, a region characterized by a high percentage of volcanics (29.1% of surface area). The presented DSi-flux model is based on data of 516 catchments, covering approximately 56.7% of the area of the Japanese Archipelago. The spatial distribution of

lithology—one of the most important first order controls—is taken from a new high resolution map of Japan. Results show that the Japanese Archipelago is a hyperactive region with a DSi-yield 6.6 times higher than the world average of 3.3 t SiO₂ km⁻² a⁻¹, but with large regional variations. Approximately 10% of its area exceeds 10 times the world average DSi-yield. Slope constitutes another important controlling factor on DSi-fluxes besides lithology and runoff, and can exceed the influence of runoff on DSi-yields. Even though the monitored area on the Japanese Archipelago stretches from about 31° to 46°N, temperature is not identified as a significant first-order model variable. This may be due to the fact that slope, runoff and lithology are correlated with temperature due to regional settings of the Archipelago, and temperature information is substituted to a certain extent by these factors. Land cover data also do not improve the prediction model. This may partly be attributed to misinterpreted land cover information from satellite images. Implications of results for Earth System and global carbon cycle modeling are discussed.

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Introduction

Silicate weathering is an important process within the global carbon cycle because soil and thus atmospheric CO₂ is ‘consumed’ by silicate weathering. On time scales of thousands to millions of years this process is capable to reduce atmospheric CO₂ concentration significantly (Kempe 1979; Kempe and Degens 1985; Berner and Kothavala 2001; Lenton and Britton 2006). Dissolved silica (DSi) flux to coastal zones is also an important factor

in the oceanic carbon cycle due to the importance of DSi as a nutrient for diatom growth (e.g., Kristiansen and Hoell 2002; Buesseler et al. 2007; Harashima 2007). Diatom abundance is linked to carbon burial rates in coastal systems and in the open ocean (Buesseler et al. 2007; Harashima 2007). DSi depletion in surface waters due to diatom DSi up-take impedes diatom blooms. Thus surface water DSi concentration constitutes an important factor for coastal waters to act as a C-sink due to carbon burial. The most important sources for marine ‘new’ DSi are rivers with an estimated proportion of 80% (Treguer et al. 1995). Because of these implications it is important for global biogeochemical cycles to predict or estimate fluvial DSi-fluxes regionally and globally.

The terrestrial silicate weathering-derived DSi is transported via rivers to coastal zones. Previous work suggests that only a few ‘first-order’ factors control these silica fluxes. These include lithology (Bluth and Kump 1994; Hartmann et al. 2007a) and runoff (Bluth and Kump 1994) as the most important factors. Chemical weathering and subsequent DSi-fluxes are also influenced by temperature (Drever and Zobrist 1992), land cover (Gislason et al. 1996; Moulton et al. 2000; Fulweiler and Nixon 2005), mechanical erosion, probably linked to relief or slope (Millot et al. 2002; West et al. 2005; Lyons et al. 2005), as well as lakes and dams because they provide sediment burial sites for diatom opal (amorphous Si = ASi) (Humborg et al. 2002, 2006). The process of ASi deposition within fluvial systems is enhanced by eutrophication providing P and N for excessive diatom blooms (Turner et al. 2003).

Hyperactive areas and hot spots of silicate weathering have recently received attention due to their link to the global C cycle (cf. Gaillardet et al. 1999; Dessert et al. 2003). Hyperactive areas are classified as regions exceeding five times and hot spots as areas exceeding ten times world average yields (Meybeck et al. 2006). For semi-enclosed regional seas (Meybeck et al. 2007) riverine inputs are the most significant source of new DSi as shown for regional seas adjacent to Japan, i.e., the East China Sea, the Sea of Japan and the smaller Seto Inland Sea. DSi river input to these seas is approximately 74, 83 and 97%, respectively (considering river input, atmospheric deposition and marine intrusion as being 100%), with some uncertainty in the estimate of marine intrusion (Chen et al. 2004; Hartmann et al. 2007b). Because of missing data, ASi was not considered in these budgets.

One strategy to estimate DSi-fluxes to coastal areas are measurements at the river outlets. Unfortunately only few data are available for the large world rivers (Garnier et al. 2006). The largest published global, representative data base lists DSi-fluxes for 215 rivers (Meybeck and Ragu 1995). Global average concentrations of DSi were investigated, e.g., by Garnier et al. (2006) and Meybeck (2005).

Up to now global or regional models predicting river DSi-fluxes are still missing. However, previous models of global and regional riverine fluxes of alkalinity, organic carbon, suspended matter as well as N and P showed that it is possible to predict these fluxes based on empirical functions derived from training data sets (Ludwig et al. 1996; Verstraeten and Poesen 2002; Amiotte-Suchet et al. 2003; Bouwman et al. 2005; Seitzinger et al. 2005; Beusen et al. 2005; Verstraeten 2006; Syvitski and Milliman 2007). The regional scale is defined as ranging from 10^4 to 10^7 km² as suggested by IPCC (Root et al. 2005). Derived empirical or statistical prediction functions from previous works use geodata representing characteristics such as runoff, lithology and land cover of each watershed and water quality data for model calibration. Some approaches use statistical approaches like multiple linear regression or nonlinear regression to develop lumped models. Models are sometimes enhanced by mechanistical components for spatial explicit application (Seitzinger et al. 2005). Mechanistical components are in general not based on functions identified from analysis of training data.

In addition, entirely process-based models of DSi-fluxes for individual rivers, emphasizing instream biogeochemical processes, were developed (Garnier et al. 2002, 2006; Sferratore et al. 2005). Because a large number of parameters have, however, to be adjusted for each river system, these models are not easily applicable to larger scales. Simple transfer of existing models to other river systems is constrained by differences in climate, internal geomorphical structure (e.g., river bed morphology, etc.), ecosystem structure, anthropogenic influence, as well as the extent of available databases for parameterization. Specifically, the estimates of DSi-fluxes into a river system are based on river budgets.

Global hyperactive regions and hot spots of natural river DSi-fluxes were recently identified by Dürr et al. (2008) based on data from Meybeck and Ragu (1995) applying a budget approach. Accordingly, the world average concentration is around 9.5 mg SiO₂ l⁻¹ and the specific SiO₂ yield 3.3 t km⁻² a⁻¹. The global budget approach by Dürr et al. (2008) is based on cluster effects between relevant first-order controls of DSi-fluxes (lithology, climate, catchment area and runoff). This simplified budget approach indicates that large regions, characterized by flood basalts and volcanic arcs, and specifically humid regions, located in the “Ring of Fire” around the Pacific, are at least hyperactive areas of DSi-fluxes. Pacific catchments contribute 32% to the global exorheic (draining to the oceans) DSi-fluxes, while they occupy only 17% of the global exorheic, non-glaciated landmass.

To our knowledge, an empirical DSi-flux model for a regional hyperactive or hot spot multiple river area does not yet exist. One important precondition for such a model

is the existence of a large data set of river DSi-fluxes. Such a data set exists for Japan based on the extensive work of Kobayashi (1960) from the 1940s to 1970s, covering more than 750 sampling locations (Fig. 1). Here we introduce a new process-based, lumped model approach with application to the Japanese Archipelago applying previous findings about local and regional scale processes and integrating ‘first-order’ controlling factors on DSi-fluxes.

The present work is organized as follows: available data, their quality and the data analyzing techniques and a preview of data are given. Specifically, for this study a new vector-based lithological map of Japan was developed, incorporating 12 major lithological classes with respect to weathering sensitivity, as developed at the global scale by Dürr et al. (2005). A brief overview of the typical Japanese regional settings is provided, i.e., lithology, river systems, climate and other important factors. In addition, observed DSi-fluxes and model results are reviewed. Influences of proposed first-order controls on DSi-fluxes are discussed. Implications for modeling of the global carbon cycle are discussed.

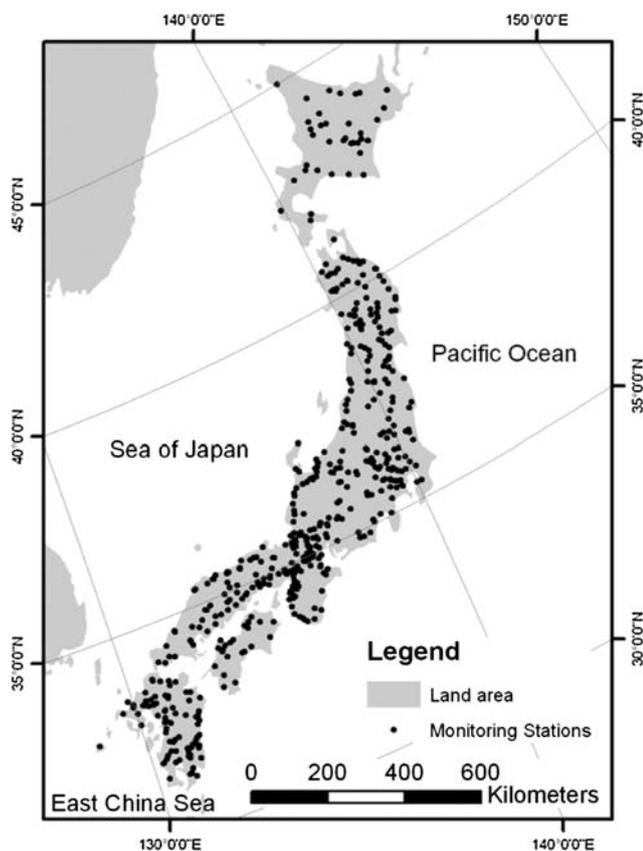


Fig. 1 Main islands of the Japanese Archipelago and sampling locations at river sites used for modeling. Islands in the southwest were cut out for better presentation and no sampling location from this area was used in this study

Data handling and analysis techniques

Hydrochemical data and geodata handling

Documents containing the summary of the work of Kobayashi (1960) were untouched and forgotten for nearly two decades in a warehouse at Okayama University, Japan (cf. Harashima et al. 2006). They contain hydrochemical data of Japanese rivers for 754 sampling locations from basically two sampling periods: 1940/50s and 1970s. In general, 6–12 samples per year and sampling location were taken to represent DSi seasonality. Anthropogenic contamination was avoided, if possible, by using sampling sites upstream of urbanized regions. These data were digitized from the hand-written tables.

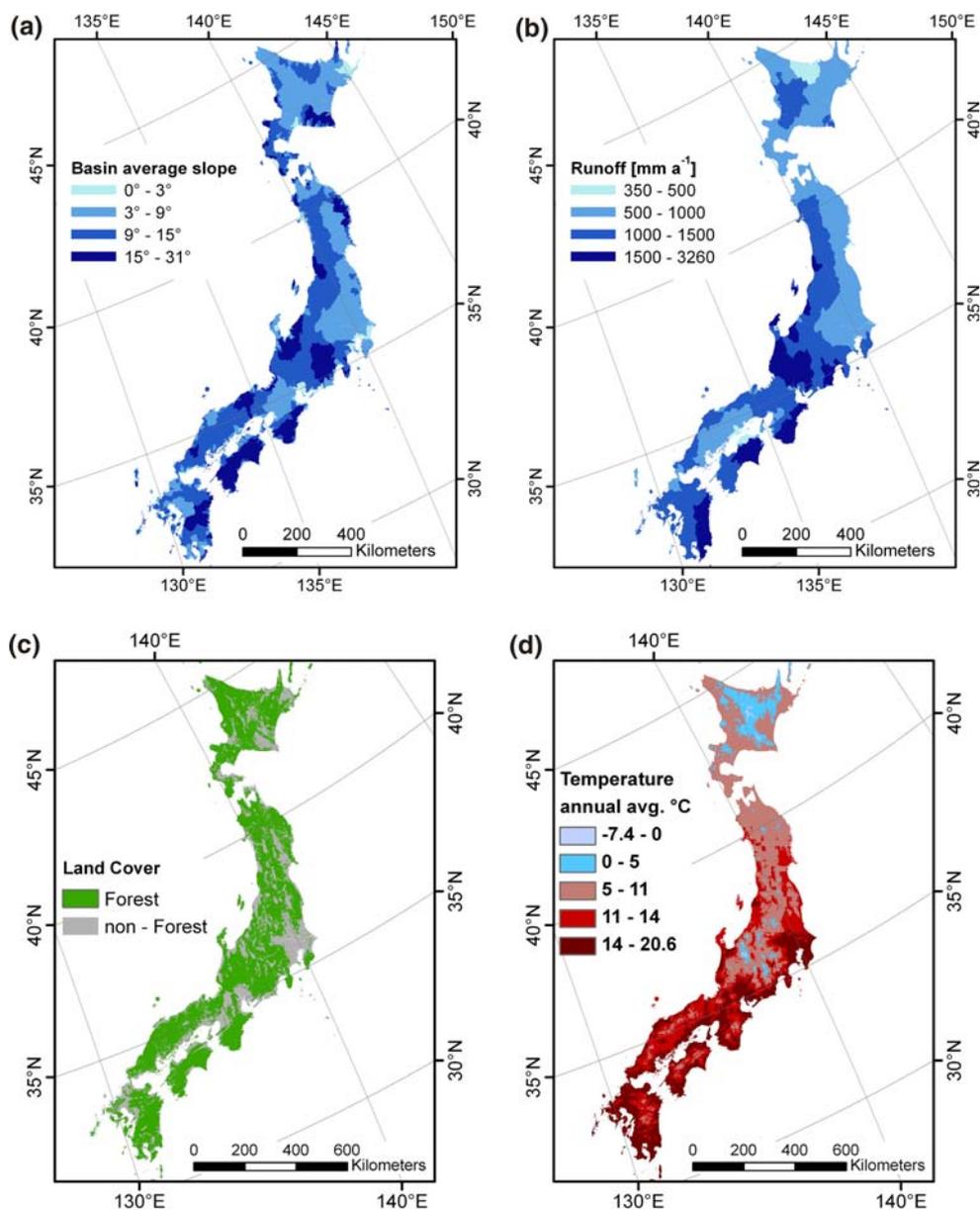
The 1970s data were omitted if those of the 1940/50s were available in the immediate vicinity. Sampling locations were discarded if the following quality criteria were not met: (1) every sample of the location shows a chloride concentration $\leq 30 \text{ mg l}^{-1}$ (to rule out seawater intrusion, anthropogenic contamination and hydrothermal activity); (2) the sample location lies at one distinct river as defined by the river system model derived from the SRTM digital elevation model (see below). In total, 238 sampling locations were omitted for not fully satisfying these criteria. The remaining 516 locations (each defining a catchment) were used for the analysis here and are located in 240 different river basins draining to the Sea of Japan, Seto Inland Sea, the East China Sea or to the Pacific Ocean (Fig. 1).

SRTM digital elevation model (DEM) data from the International Center of Tropical Agriculture (CIAT) (2004) were used to calculate the catchment areas represented by the sampling locations, elevations, slope and flow direction on a grid resolution of $100 \times 100 \text{ m}$, using the GIS software ArcGIS 9.2 (ESRI). The sum of all catchment areas covers about 56.7% of the considered area of the Japanese Archipelago ($213,467 \text{ km}^2$). Average slope of catchments are provided in Fig. 2a.

Runoff data with a spatial resolution of 0.5° from UNH/GRDC Composite Runoff fields V1.0 (Fekete et al. 2002) were applied to calculate annual runoff from each catchment (Fig. 2b). The total specific DSi-flux for each catchment was obtained by multiplying annual runoff with the annual average DSi concentration (Fig. 3a). Applied runoff data were successfully compared for plausibility with runoff data of approximately 150 catchments provided in Kobayashi (1960).

The digital vector-based geological map of Japan (Geological Survey of Japan 2003) was used to develop a new lithological map of Japan (Fig. 4), applying lithological classes introduced by Dürr et al. (2005). These classes incorporate information on average mineral proportions

Fig. 2 Average slope and runoff of Japanese river basins are provided in **a** and **b**. Land cover forest distribution is the dominating land cover class on the Japanese Archipelago (**c**). Second dominant ones are agricultural areas; urban land cover is surprisingly only minor according to applied land cover data (Table 1). Elevation corrected temperature distribution on the Japanese Archipelago reflects regional landscape elevation (**d**). Figures are from Hartmann (2008)



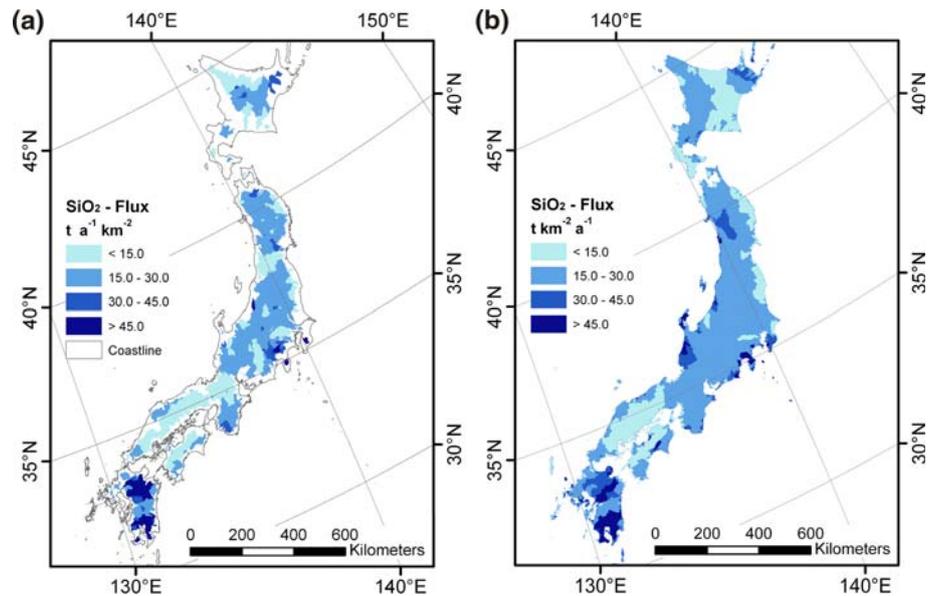
and further lithological properties important to study weathering processes. Pyroclastic Flows (PY) was introduced as an additional lithological class. It includes unconsolidated, young volcanogenic sediments with a considerable porosity and high relevance for silicate weathering (compare Okuda et al. 1995). The number of classes was eventually reduced to 12 (Table 1) because the others were not of relevance to the geological setting of Japan (Takai et al. 1963). Relative proportions of each lithological class were calculated for each catchment using ArcGIS 9.2.

Sizes of land cover classes were calculated for each catchment based on the Land Cover Data for Central Asia

(Tateishi et al. 2003) with resolution of 200×200 m (Fig. 2c, Table 1). Even though the land cover data are representative of the year 2000, it is assumed that there are only small differences compared to the time of water sampling. Urbanized areas of Japan comprise only a small proportion of the total area, and land use class proportions, specifically for forests and crop/rice did not change much. An exception could be regions dominated by unconsolidated sediments, where most human activity is concentrated. A cross-check with older maps was conducted but not many differences for most regions were detected.

Temperature data (resolution 10') from the International Water Management Institute (2000) were applied to

Fig. 3 Calculated DSi-fluxes of catchments defined by the sampling locations after Kobayashi are given in **a**. Modeled DSi-fluxes are shown in **b**. Only 37 catchments of the modeled DSi-fluxes (**b**) are characterized by specific DSi-fluxes lower than world average. They cover only 162.9 km², which is 0.4% of the total land area of the Japanese Archipelago



calculate average annual temperature for each basin. Furthermore temperature was corrected by -0.0053 K m^{-1} altitude to represent elevation differences (cf. Schmarnow et al. 1982). The difference between actual SRTM altitude and elevation of each original temperature grid cell ($10'$) was used to calculate the elevation corrected mean temperature. Results were visually evaluated and even though grid boundaries are still visible, elevation corrected data (based now on the SRTM grid resolution) are now approaching each other at grid boundaries (Fig. 2d).

Atmospheric silica deposition was calculated using twelve stations representing the regional differences within Japan. Data were interpolated and average DSi atmospheric deposition rates for each catchment were calculated by applying regionalized precipitation data from over 150 atmospheric deposition monitoring stations using the product of precipitation and calculated local DSi concentration in atmospheric deposition. References for data used are given in Appendix A.

Soil data information for Japan with a resolution of $5'$ were derived from Batjes (2006).

DSi-flux modeling technique

The analysis of the data used and the modeling workflow is schematised in Fig. 5. Calculated DSi-fluxes for each of the 516 catchments did not show large differences between observed (uncorrected) fluxes and fluxes corrected for atmospheric deposition. Because this difference represents only 2% of observed fluxes the originally observed fluxes were maintained for further analysis. This

decision is based on the possibility that our model framework may be applied to global modeling later because the normally provided hydrochemical data sets are not corrected for atmospheric silica deposition. However, in the future the relevance of the global contribution of atmospheric DSi to river DSi should be investigated more closely. In a first approach (Treguer et al. 1995) estimated it to be around 10%.

After calculating the areal average of assumed 'first-order' controls according to the literature (i.e., runoff, temperature, slope, elevation, and proportion of lithological classes, land cover classes and soil characteristics (pH, soil depth and soil organic C content) for each of the 516 catchments correlation analysis was carried out between them and specific DSi-fluxes ($\text{t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$) for catchments dominated by one lithological class (i.e., one class covering $>60\%$ of the catchment area).

In addition, scatter plot analyses were used to detect significant linear or nonlinear relationships between assumed first-order controls and DSi-fluxes. In this way lithology, runoff, slope and temperature were identified as potential predictors within the emphasized empirical model. Even though temperature correlates in general with slope (due to increasing slope in areas of high elevation) it does not show a clear correlation with DSi-flux for most lithological classes. Scatter plots relevant for analysis are presented in Appendix B.

Based on the results of the pre-analysis, several multi-variable prediction functions for specific DSi-flux were tested, using the total data set of 516 catchments. Specifically, three prediction equation types were tested to calculate specific flux (SF) of DSi:

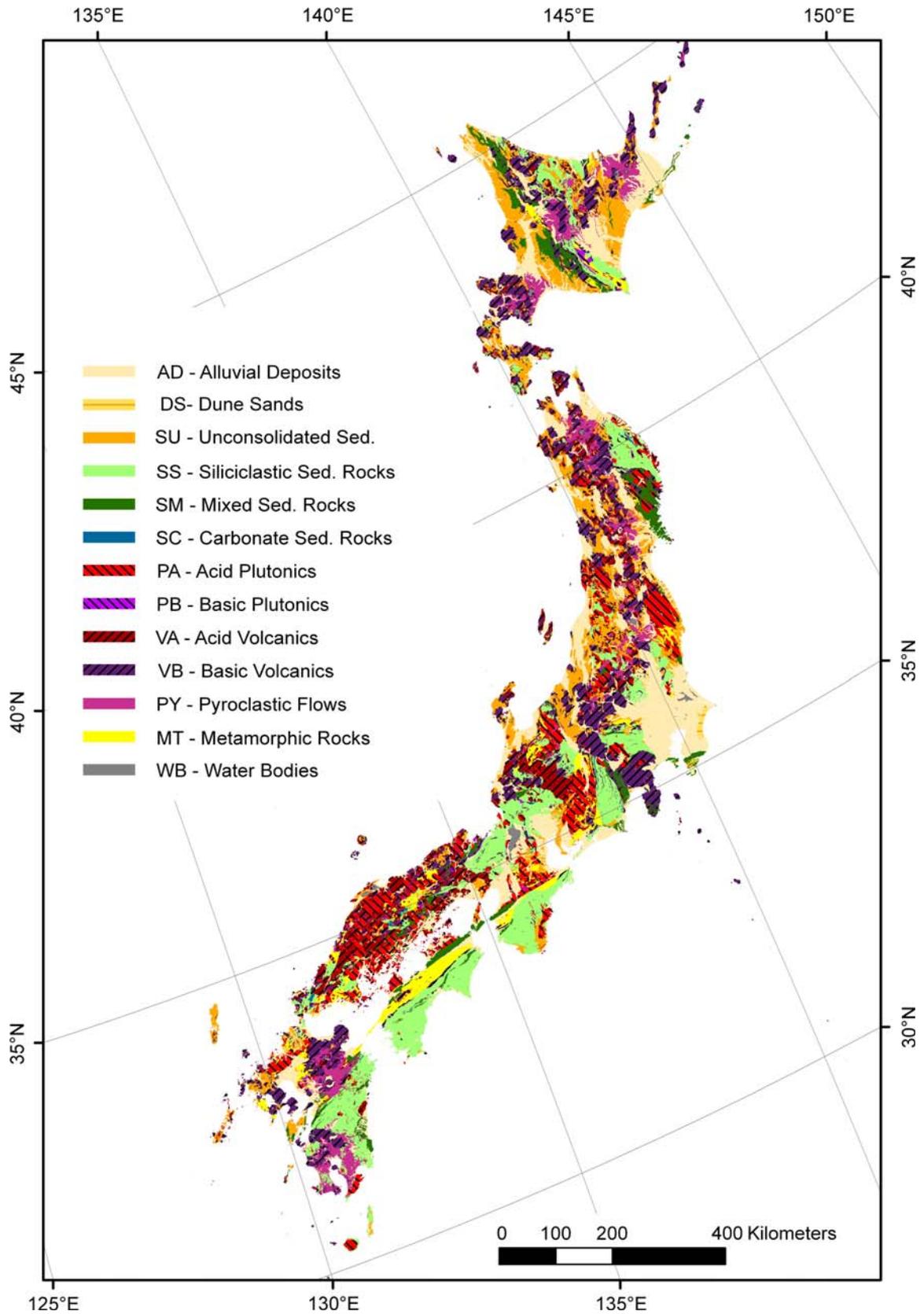


Fig. 4 Lithological map of Japan, derived from the vector-based geological map of Japan (1:1,000,000) (Hartmann 2008)

Table 1 Catchment properties of monitored catchments used in analysis are compared with areal properties of the Japanese Archipelago

	Monitored watersheds				All Japan basins				Lithology of global basins				Monitored catchments with a proportion of one lithological class >70%				Monitored catchments with a proportion of one lithological class >60%								
	Properties of all 516 catchments		SiO ₂ -flux (t SiO ₂ km ⁻² a ⁻¹) from watersheds holding >70% of one lithological class		Mean	Max	Min	Standard deviation	60 largest rivers applied by Gaillardet et al. (1999)	Other river basins not considered by Gaillardet et al. (1999)	Slope (°)	Runoff (mm a ⁻¹)	Flux (t SiO ₂ km ⁻² a ⁻¹)	n	Slope (°)	Runoff (mm a ⁻¹)	Flux (t SiO ₂ km ⁻² a ⁻¹)	n							
	Mean	Max	Min	Standard deviation							Min	Max	Min	Max	Min	Max	Min	Max							
SiO ₂ flux (t SiO ₂ km ⁻² a ⁻¹)	20.6	85.3	4.5	15.1	21.8	355.2	0.0	18.3																	
Catchment area (km ²)	3062	9791	0.5	1343	4880	20421	1.0	480																	
Slope (°)	13.0	29.0	0.4	4.9	11.0	28.2	0.1	5.6																	
Temperature (°C)	10.0	18.2	0.5	3.2	10.7	20.6	-7.4	1.7																	
Forest (%)	74.37	100	0.0	22	69.27	100	0	38																	
Cropland (%)	24.24	100	0.0	21	27.86	100	0	38																	
Urban (%)	0.22	50	0.0	3	0.51	100	0	2																	
Rice (%)	0.56	13.50	0.0	1	0.99	100	0	5																	
Runoff (mm)	1096	3263	414	465	1104	3263	351	411																	
Alluvial deposits (AD)	14.89%	100%	0%	19.0%	20.9	20.97%	100%	0%	36%	16.3%	15.3%	0.4	6.2	600	1431	7.5	57.5	15	0.4	8.4	600	1431	7.5	57.5	17
Dune sediments (DS)	0.00%	0%	0%	0.0%	0.14%	100%	0%	4%	0.23%	1.71%															
Metamorphic rocks (MT)	4.37%	100%	0%	12.2%	3.94%	100%	0%	13%	2.3%	4.9%	13.2	27.3	490	1756	5.1	14.3	5	10.5	27.3	490	1756	5.1	14.9	6	
Acid plutonics (PA)	11.13%	100%	0%	21.3%	10.16%	100%	0%	24%	3.7%	7.7%	5.9	29.0	625	1804	9.4	33.3	24	13.0	5.9	625	1804	9.4	33.3	29	
Basic-ultrabasic plutonics (PB)	0.78%	24%	0%	2.5%	0.73%	100%	0%	6%	0.12%	0.29%															
Pyroclastic Flows (PY)	7.75%	100%	0%	15.9%	5.41%	100%	0%	12%			5.9	8.9	743	1564	18.9	81.0	3	5.9	14.4	663	1580	19.9	85.3	11	
Carbonate rocks, consolidated (SC)	0.29%	28%	0%	2.0%	0.21%	100%	0%	3%	15.3%	11.6%															

Table 1 continued

	Monitored watersheds				All Japan basins				Lithology of global basins		Monitored catchments with a proportion of one lithological class >70%				Monitored catchments with a proportion of one lithological class >60%										
	Properties of all 516 catchments				SiO ₂ -flux (t SiO ₂ km ⁻² a ⁻¹) from watersheds holding >70% of one lithological class				60 largest rivers applied by Gaillardet et al. (1999)		Other river basins not considered by Gaillardet et al. (1999)		Slope (°)		Runoff (mm a ⁻¹)		Flux (t SiO ₂ km ⁻² a ⁻¹)		Slope (°)		Runoff (mm a ⁻¹)		Flux (t SiO ₂ km ⁻² a ⁻¹)		
	Mean	Max	Min	Standard deviation	Mean	Max	Min	Standard deviation	Mean	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
Mixed sedimentary rocks (SM)	2.75%	95%	0%	11.2%	12.8	4.42%	100%	0%	21%	5.4%	7.6%	13.7	18.6	414	1203	7.5	17.5	5	11.8	18.6	414	1203	7.5	17.5	6
Siliclastic sedimentary rocks (SS)	19.32%	100%	0%	31.3%	17.6	16.17%	100%	0%	31%	15.4%	13.8%	7.3	25.6	625	2493	8.4	43.0	67	7.3	25.6	449	2493	5.3	43.1	87
Sediments, semi- to unconsolidated (SU)	10.34%	96%	0%	15.2%	25.9	13.54%	100%	0%	30%	11.4%	8.8%	8.3	15.2	1115	2180	15.7	54.0	6	8.3	17.0	511	2180	12.9	54.0	13
Acid volcanics rocks (VA)	8.09%	100%	0%	15.0%	17.0	6.66%	100%	0%	18%	0.35%	0.90%	10.3	17.3	864	3263	8.1	48.1	7	10.2	17.3	864	3263	8.1	48.1	11
Basic and intermediate volcanic rocks (VB)	19.58%	100%	0%	20.8%	28.6	17.00%	100%	0%	37%	7.3%	6.9%	7.7	20.0	495	2643	16.2	57.6	16	7.7	20.0	495	2643	16.2	57.6	24
Water (WB)	0.72%	27%	0%	1.7%		0.63%	38%	0%	1%	0.55%	0.77%														
Loess										4.0%	1.5%														
Complex lithology										5.7%	6.6%														
Precambrian basement										10.3%	9.6%														
Evaporites										0.01%	0.21%														
Polar ice and glaciers										0.00%	1.8%														

Additional information on slope, runoff and SiO₂-yield are in °, mm a⁻¹ and t SiO₂ km⁻² a⁻¹, respectively. 516 catchments were used from the Kobayashi data set, and the number of exorheic basins is 7,871. In addition information on minima and maxima for slope, runoff and specific DSI-fluxes for each lithological class (if holding a proportion of more than 60 and 70 % per monitored catchment) are given for catchments defined by sampling locations of Kobayashi, used in this study. These values are used to estimate the range for which the derived multi-lithological model function is valid. The total number of catchments in each section is given as *n*. Due to misinterpretation of land cover, crop might contain a large proportion of rice paddy and vegetable fields (for further discussions see Frey and Smith 2007). For comparison lithological proportions in 60 large river basins after Gaillardet et al. (1999) and the remaining rivers of the world are given. Their lithological proportions are calculated based on a global lithological map (Diirr et al. 2005) and using the global elevation model hydrok

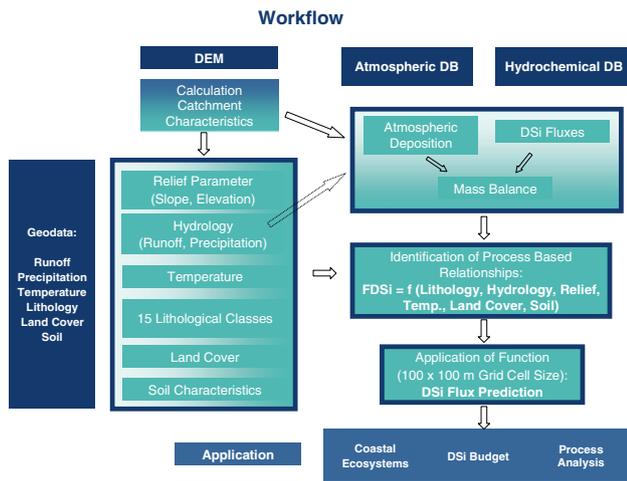


Fig. 5 General workflow of the modeling framework. Note that due to the small contribution of atmospheric deposition, uncorrected river DSI-fluxes were used for modeling

$$SF(DSi) = b_0(L_1s^{b_{11}}q^{b_{12}} + L_2s^{b_{21}}q^{b_{22}} + \dots + L_ns^{b_{n1}}q^{b_{n2}}) \quad (1)$$

$$SF(DSi) = b_0(L_1s^{b_{11}} + L_2s^{b_{21}} + \dots + L_ns^{b_{n1}})q^{b_1} \quad (2)$$

$$SF(DSi) = b_0(b_1L_1 + b_2L_2 + \dots + L_n)q^{b_q}s^{b_s} \quad (3)$$

L_x is the proportion of each lithological class x in a catchment, s represents the average slope in degrees and q the average runoff in mm a^{-1} . b_{xy} are parameters which were estimated by nonlinear regression analysis using the Levenberg–Marquardt technique, implemented in the statistical software package Statistica 8.0 (Statsoft).

Note, that in lithologically heterogeneous regions, like Japan, a mono-lithological approach (one lithology representing the catchment) is bound to fail, as only a few watersheds are characterized by one lithology. Even the number of catchments being at least dominated by one lithology (i.e., reaching 60–70% of the catchment area) is very low (Table 1). The idea of the ‘multi-lithological’ lumped model approach is to estimate the contribution of each lithological class to total catchment DSI-fluxes according to identified first-order controls (i.e., predictors).

The design of the equations for the lumped multi-lithological model is process based, incorporating knowledge from previously identified relationships between potential controlling factors and DSI-fluxes (see “Discussion”). Basically the positive correlation between runoff and specific DSI-fluxes, previously reported by Bluth and Kump (1994) for other regions, was included, emphasizing differences for each lithological class. Slope, for example is in general inversely correlated with DSI-fluxes in catchments

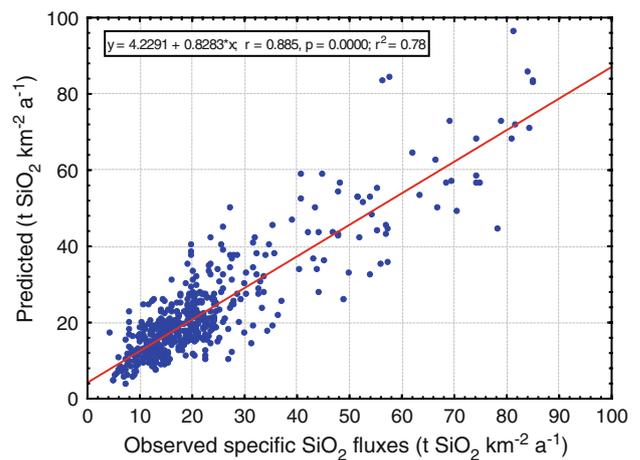


Fig. 6 Observed versus predicted specific DSI-fluxes for the 516 catchments using the averages of the calculated b_{xy} parameters after conducting 1,000 times random sampling are presented (Table 2)

because with increasing slope, reaction rates per volume of water with mineral surfaces or influence of biology are decreasing.

We also tested variations of Eqs. 1–3, to include temperature, represented by an Arrhenius-term ‘ $e^{(b_T T)}$ ’, and land cover proportion, or to substitute slope by one of these. However, only for two functional relationships tested (Eq. 1 and 2), all estimated b-parameters passed test statistics according to the 5% significance criterion. The highest correlation coefficient ($r = 0.88$) between predicted and observed fluxes (Fig. 6) is achieved by Eq. 1. All lithological classes listed in Table 1 were included into the prediction equations with the exception of dune sands, carbonates and basic plutonic rocks, as their proportion on the training catchments is very small only (0.0, 0.4 and 0.8%, respectively). Including them caused additional noise and the quality of the model decreased.

To evaluate the significance of the identified functional relationship, random sampling of the 516 catchments and their properties lithology, runoff and slope was carried out, choosing each time 80% of the total data set. The b -parameters were recalculated 1,000 times according to Eq. 1 in this way. Resulting average b_{xy} -parameters (Table 2) were then applied to predict DSI-fluxes on exorheic catchments of Japan. These catchments and their properties were calculated using ArcGIS 9.2. In total, 122,000 basins were differentiated, but most are very small, located along the coastlines. For technical reasons, all those coastline basins ($\sim 114,000$) with $<1 \text{ km}^2$ were combined into one catchment representing 3.2% of the total area of the Japanese Archipelago; 7,871 larger basins remained.

Table 2 Average estimated *b*-parameters for runoff and slope after 1,000 times random sampling of the data set

	Mean	Median	Standard deviation	Minima	Maxima	25th%	75th%	Valid <i>n</i>
b0	0.05	0.05	0.01	0.02	0.12	0.04	0.06	1,000
AD slope b11	−0.07	−0.06	0.05	−0.28	0.03	−0.09	−0.03	1,000
AD runoff b12	0.88	0.88	0.04	0.74	1.02	0.86	0.91	1,000
MTslope b21	−0.81	−0.78	0.22	−1.63	0.23	−0.87	−0.70	1,000
MTrunoff b22	1.05	1.04	0.08	0.65	1.35	1.01	1.08	1,000
PA slope b31	−0.01	−0.01	0.08	−0.27	0.34	−0.06	0.04	1,000
PA runoff b32	0.83	0.83	0.05	0.65	1.01	0.80	0.86	1,000
Py slope b41	−0.35	−0.35	0.09	−0.73	−0.14	−0.40	−0.29	1,000
Py runoff b42	1.11	1.11	0.04	0.99	1.26	1.08	1.13	1,000
SM slope b51	−2.06	−2.13	1.47	−44.09	1.16	−2.29	−1.92	1,000
SM runoff b52	1.60	1.64	0.40	0.39	12.12	1.55	1.69	1,000
SS slope b61	−0.84	−0.84	0.14	−1.30	−0.34	−0.93	−0.75	1,000
SS runoff b62	1.12	1.13	0.06	0.89	1.31	1.09	1.17	1,000
SU slope b71	−0.12	−0.13	0.19	−0.84	1.81	−0.22	−0.04	1,000
SU runoff b72	0.86	0.87	0.09	0.04	1.08	0.81	0.91	1,000
VA slope b81	−1.18	−1.06	0.56	−4.62	2.43	−1.21	−0.96	1,000
VA runoff b82	1.21	1.17	0.21	−0.17	2.48	1.13	1.21	1,000
VB slope b91	−1.26	−1.25	0.16	−2.09	−0.77	−1.36	−1.15	1,000
VB runoff b92	1.35	1.35	0.07	1.15	1.72	1.31	1.40	1,000

For comparison median, standard deviation, minima, maxima and quartiles are given. Each parameter is significant on the 5% *p* value and *b*-parameters are normally distributed in each case, indicated by the narrow ranges between mean and median values

Results

Regional settings

Japan is a typical island arc, located at the boundaries of three tectonic plates (Pacific, Eurasian and the Philippine). It is characterized by high proportions of volcanic rocks (classes VA, VB, PY, see Table 1). Acid plutonics (PA), siliciclastic sedimentary rocks (SS) and unconsolidated sediments (AD and SU) are other major lithological classes. Carbonate rocks occur on only 0.3% of the area. The average slope of the exoreic basins is 11°, with maximal values of about 29° in areas characterized by high proportion of sandstones, volcanics, plutonics or metamorphics. Properties of the 516 training catchments are only slightly different from those of the entire Japanese Archipelago, and hold an average slope of 13°. According to the land cover data used here, Japan is covered to 69.3% of forests, 27.9% of crop land, and a surprisingly small proportion of rice fields (1%) and urbanized areas (0.5%). A discussion on land cover distribution is provided below. For the 516 training catchments, land cover proportions are 74.4, 24.2, 0.6 and 0.2%, respectively. The average runoff amounts to 1104 mm a^{−1}, with maxima of up to 3,200 mm a^{−1} in regions of Honshu facing the Sea of

Japan, Wakayama (middle part of southern Honshu), East Shikoku and southeast of Kyushu.

The typical basin size of Japanese river systems is rather small and steep, with a small basin size because of the specific morphology of the Archipelago (Table 1). Residence time of the water is, therefore, low which reduces the capability of diatoms to transfer DSi into amorphous silica (ASi). Only a few larger lakes exist that could retain dissolved silica as indicated by the small area of water bodies (Table 1).

Observed DSi-fluxes

Sampling locations of Japanese rivers in this study are given in Fig. 1, representing mostly the major islands Honshu, Hokkaido, Kyushu and Shikoku. Averages for DSi-fluxes, lithology, runoff, slope, temperature and land cover and the areas covered by monitoring are listed in Table 1. The average specific DSi-flux from the 516 catchments (20.6 t SiO₂ km^{−2} a^{−1}) is 6.2 times higher than the world average (3.3 t SiO₂ km^{−2} a^{−1}), underlining that Japan is hyperactive with respect to DSi-fluxes. Atmospheric contribution of soluble Si is minor if compared to DSi mobilized by weathering (2% of fluvial DSi-fluxes). This low proportion—if compared to global estimates of

10% (Treguer et al. 1995)—can be attributed to the high weathering rates of Japan.

Relations between proposed first-order controls and DSi-fluxes

The dominant influence of lithology is revealed by average specific DSi-fluxes for catchments with one dominant (i.e., >70% of area) lithological class (Table 1). Highest specific DSi-fluxes are found for catchments dominated by volcanics and unconsolidated sediments (Appendix B). For volcanics this is in accordance with previous research on weathering rates (Dessert et al. 2003; Rad et al. 2006).

Univariate correlation and scatter plot analyses between first-order controls and DSi-flux for each lithological class revealed that for most classes reliable functional relations with DSi-fluxes exist only for runoff and slope (Appendix

B). Regressions plotted in Appendix B are influenced by noise of other lithological classes characterized by different specific DSi-fluxes. While runoff shows a positive correlation with DSi-fluxes for each lithological class (caused in part by including runoff in the flux calculation), relations between DSi-flux and slope are characterized by a negative regression for most lithological classes as would be expected. In case of positive regressions (lithological classes AD, SS, PA and SM), correlation coefficients were not significant on the *p* level of 15%. For some relations with a positive correlation between slope and DSi-fluxes, like mixed sedimentary rocks (SM), and admixture with ‘contamination’ due to significant amounts of volcanics is the explanation. Negative correlation is observed after omitting catchments showing significant proportions of volcanics for the class SM. Note, that volcanic classes PY and VB are in general characterized by high specific DSi-fluxes.

Fig. 7 Specific DSi-fluxes for fixed slope and variable runoff for mono-lithological conditions. DSi-fluxes were calculated using the *b*-parameters estimated by Eq. 1 (Table 2), based on the principal equation $F(\text{DSi}) = b_0 s^{bs} q^{bq}$, where *s* is slope, *q*, runoff, *bs* the parameter for slope and *bq* the parameter for runoff. Typical slope ranges (rounded to next 5°) for each lithological class if its areal proportion is higher than 60%. VB 5–25°; PY 5–15°; VA 10–20°; MT 10–30°; PA 5–30°; SM 10–20°; SS 5–30°; SU 5–20°; AD 5–15°. Note that the scales for DSi-flux are different for each figure. Full names of lithological class abbreviations are supplied in Table 1

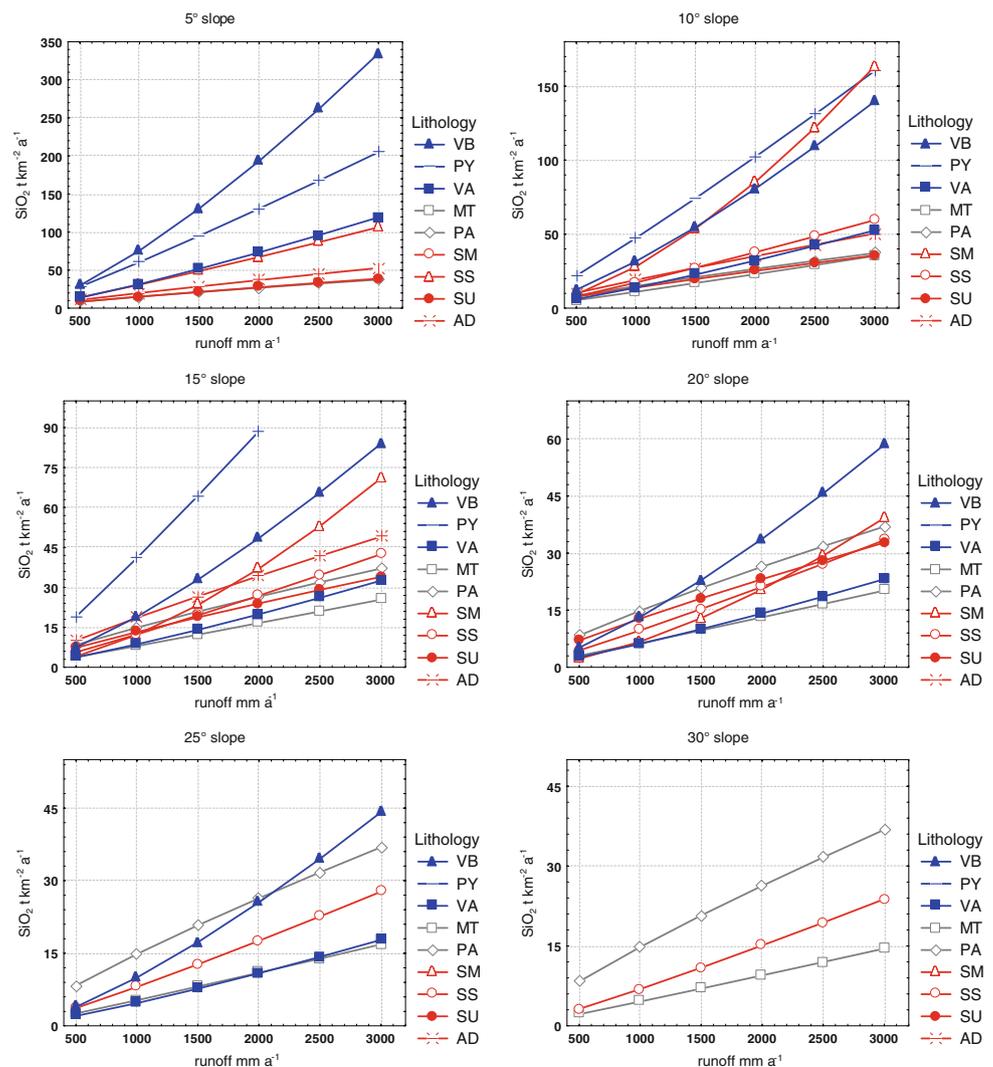
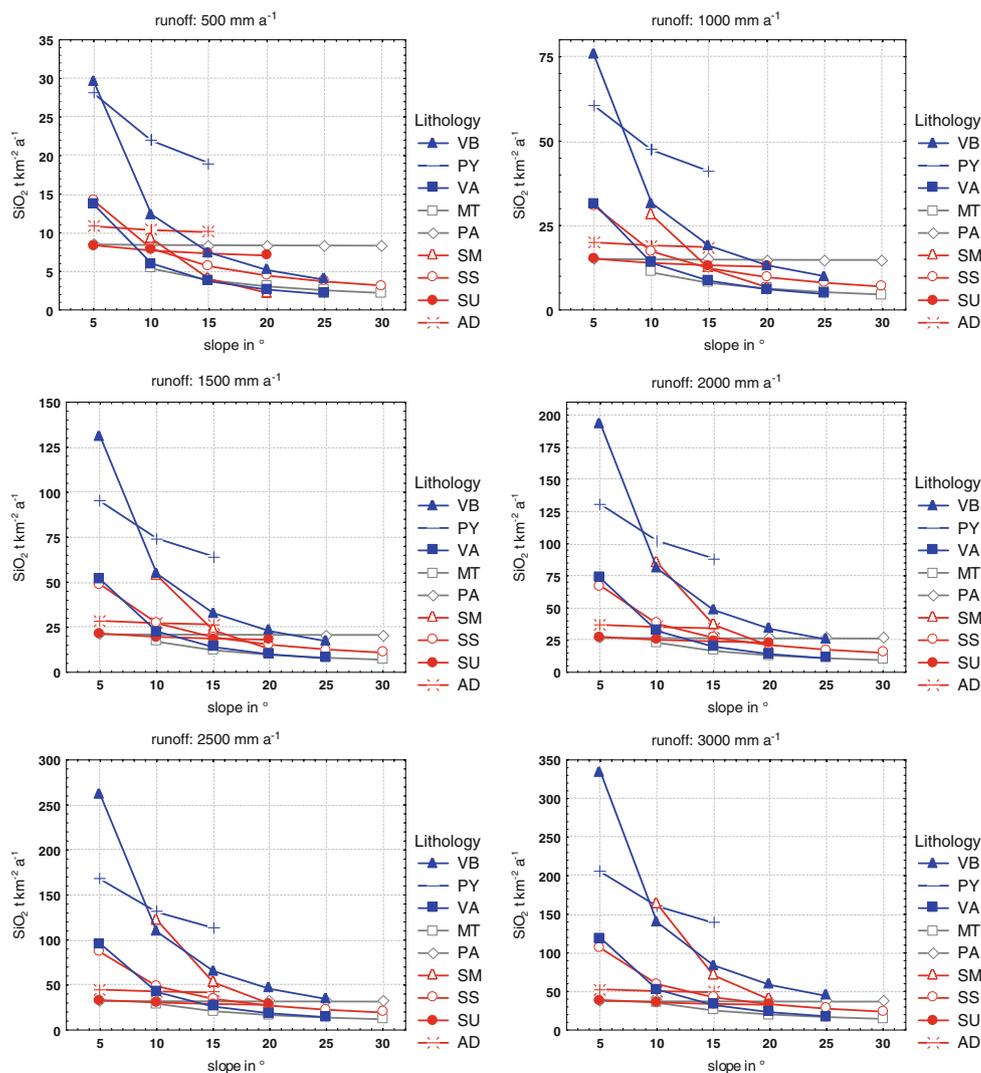


Fig. 8 Specific DSi-fluxes for fixed runoff and variable slope for mono-lithological conditions. DSi-fluxes were calculated using the b -parameters estimated by Eq. 1 (Table 2) based on the principal equation $F(\text{DSi}) = b_0 s^{bs} q^{bq}$, where s is slope, q , runoff, bs the parameter for slope and bq the parameter for runoff.

Typical slope ranges (rounded to next 5°) for each lithological class if its areal proportion is higher than 60%. VB 5–25°; PY 5–15°; VA 10–20°; MT 10–30°; PA 5–30°; SM 10–20°; SS 5–30°; SU 5–20°; AD 5–15°.

Note that the scales for DSi-flux are different for each figure. Full names of lithological class abbreviations are supplied in Table 1



Some individual temperature and DSi-flux correlations proved to be significant; others were not because of too many outliers. The significant multiple correlation of temperature with slope and runoff (Figs. 7, 8), suggests that temperature can be substituted in part by these two factors (Fig. 9). Specifically in elevated areas slope and temperature correlate highly.

Other factors, such as land cover and soil characteristics did not show significant univariate correlations and/or clear patterns with specific DSi-fluxes for the majority of lithological classes. Often scatter plot analysis revealed complex patterns, indicating some irregular influence as for example in case of forest proportion (Fig. 10a). Thus, no basic functional relationship exists for these factors in form of a simple term in a prediction equation. Note, that ‘first-order’ controls in prediction equations can only be parameters with previously identified significant correlations and applicable functional relations that were accepted after pre-analysis. In

addition, a detailed analysis of land cover reveals that specifically in elevated regions of Honshu, crop and rice fields are not always represented appropriately. For example, in elevated areas of the Japanese Alps sometimes crop is displayed as land cover where no agricultural activity is evident from satellite images or maps. For further discussion about this problem on recent land cover data see Frey and Smith (2007).

These results show that the mono-lithological approach would leave only a few catchments for analysis, and additional ‘noise’ due to other first-order factors would be the consequence. Therefore, the proposed ‘multi-lithological’ approach is necessary.

Predicted DSi-fluxes: the control of runoff and slope

According to the estimation technique, prediction equations should only be applied if catchments or basin characteristics for slope or runoff are within the typical

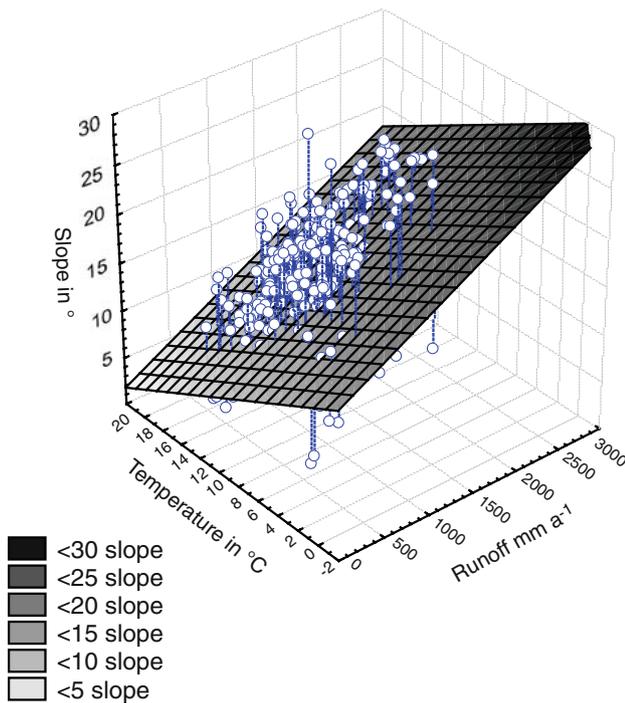


Fig. 9 A significant multiple linear correlation exists between slope, runoff and temperature for the 516 analyzed catchments ($r = 0.56$)

ranges for each lithological class. To retain appropriate ranges for slope and runoff, minima and maxima of average slopes and runoff values for each training catchment were reviewed for the case that one lithological class holds more than 60% proportion of a catchment (Table 1). Identified minima and maxima are assumed here to represent valid ranges for prediction Eq. 1 in the first instance.

Very low b -parameters indicate (Table 2) that specific DSi-fluxes are sensitive to slope, specifically for lithological classes SM, VB and VA. For a slope $<7^\circ$, specific DSi-fluxes of VB and SM are exceeding those of pyroclastics for runoff >500 mm (Figs. 7, 8). For a number of reasons, including mineral composition, grain size and hydrogeological properties, one should assume that specific DSi-fluxes from non-pyroclastics don't exceed specific DSi-fluxes from pyroclastics, under similar runoff and low slope conditions. Because of this, the slope-factor ($s^{b_{xy}}$) for lithological classes SM and VB in Eq. 1 was forced to be at least 7° for comparison with the 'not-forced' results. This approach is called 'forced approach' below. The total area affected by this forcing amounts to only 2.4% of the area of Japan. Runoff parameters appear not to be affected by this problem. This might be attributed to the observation that runoff b -parameters are close to 1 in most cases. Thus no forcing was applied for runoff parameters.

The total specific DSi-flux using the forced model amounts to $21.84 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$ or $8.18 \times 10^6 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$

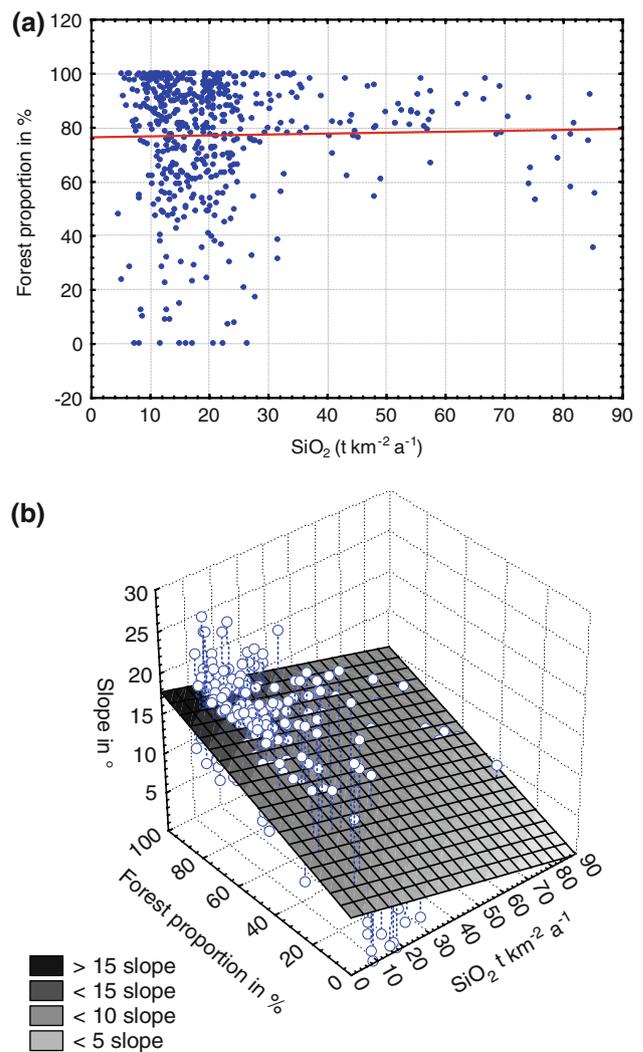


Fig. 10 Relation between specific DSi-fluxes and the land cover type forest (a), and relations between specific DSi-fluxes, slope and the land cover type forest ($r = 0.53$) (b)

as total discharge from Japan. By forcing the factor slope, 4.19% of the total modeled area is affected. An area of $37,615 \text{ km}^2$ (10% of Japan) has a specific DSi-flux of $>33 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$ and can be defined as hot spot area, according to the classification of Meybeck et al. (2007).

In case no forcing on the slope factor was applied, i.e., allowing for what we think are unreliable high specific DSi-fluxes from the lithological classes SM and VB, then the average specific DSi-flux is $23.49 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$ or $8.88 \times 10^6 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$ in total. This is 8.4% higher compared to the forced approach. In this case 19 basins show a specific DSi-flux $>1,000 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$ and eight even $>5,000 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$. Applying the forced approach, only 35 basins show $>100 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$ and six >150 with a maximum at $355 \text{ t SiO}_2 \text{ km}^{-2} \text{ a}^{-1}$. Thus,

by applying the forced approach modeled fluxes are within reported ranges from volcanic regions.

According to the process-based Eq. 1, the lumped model approach resulted in a highly significant correlation ($p < 0.0001$) between observed and predicted specific DSI-fluxes (Fig. 6). Residuals between predicted and observed specific DSI-fluxes are normally distributed, supporting the significance of the model. In addition, it was tested if temperature could be integrated into the model equation by (1) replacing slope with temperature or (2) including temperature applying a modification of the Arrhenius law (White et al. 1999; Dessert et al. 2003). In both cases correlation coefficients between predicted and observed specific DSI-fluxes were less and/or estimated b -parameters were not significant on the 5% level. Because temperature displays a multiple correlation with runoff and slope, part of the temperature information is included in the prediction equation (Fig. 9).

In Japan, a certain spatial correlation between land cover class, lithology and slope exists. However, relations between land cover and DSI-fluxes can not easily be described by simple functional relationships and information on forest is to some part incorporated in the parameter slope (Fig. 10a/b). The additional inclusion of land cover lowered the prediction quality of the model.

The mean values of retrieved b_{xy} -parameters from the model approach after sampling the data set randomly 1,000 times is given in Table 2. Higher variability of slope b -parameters (-0.01 to -2.06) compared to runoff b -parameters (0.83 to 1.6) indicates a stronger control of slope than runoff in specific cases and is discussed below. Specifically, unconsolidated sediments are characterized by comparatively high slope b -parameters (-0.35 to -0.07). Slope b -parameters close to zero are indicating that runoff is the major control in these cases. Note that for a slope b -parameter close to zero, like for AD, SU and PA the expression for slope $s^0 = 1$ may be applicable. Volcanic rocks (VB & VA) and mixed sediments (SM) are characterized by lowest slope b -parameters (< -1). In these cases less silica is mobilized with steeper slope, if runoff stays fixed.

Runoff b -parameters close to 1 (e.g., MT) indicate a nearly linear relationship between DSI-fluxes and runoff. The higher a runoff b -parameter is the higher is the influence of runoff on DSI-fluxes for a certain lithological class. Mixed sedimentary rocks (SM), acid volcanics (VA) and basalts/intermediate volcanics (VB) have lowest slope b -parameters and highest runoff b -parameters. Thus they are very sensitive to changes in one of these factors with respect to specific DSI-fluxes.

The ranges of slope and runoff b -parameters per lithological class are reflecting to some part different diagenetic settings and/or mineralogical composition and properties.

They can be divided roughly into three classes: (1) hard rocks (MT, SS), (2) volcanics (VA, VB and PY) and (3) unconsolidated (non-volcanic) sediments (AD, SU).

Figures 7 and 8 represent differences in sensitivity of DSI-fluxes due to variability in slope and runoff for each applied lithological class and the typical ranges of slope observed in the 516 catchments (compare Table 1). If runoff stays fixed the DSI-fluxes from VB and SM can exceed the ones from PY for slope values $< \sim 7^\circ$ (Fig. 8). This could be a relict from applied catchment data, as the minimum slope for catchments holding more than 60% VB and SM are characterized by a slope of 7.6° and 12° , respectively. In addition, the lithological class SM has a low areal proportion in Japan (Table 1). Predicted DSI-fluxes for not monitored catchments with slopes $< 7^\circ$ slope may thus not be within a valid range. This is supported by the observation that those of the monitored catchments that are dominated by pyroclastics normally show highest DSI-fluxes. However, it is probable that low-slope areas mapped as other volcanics have significant amounts of pyroclastics that are not mapped as individual units. Cross checking with the lithological map of Japan reveals that the areas of class SM often occur near volcanics. Thus, the estimates of b -parameters for VB and SM may be influenced by this vicinity with pyroclastics. Because of this it is important to consider valid slope ranges for each lithology. This problem is smaller for runoff, as estimated b -parameters are in general close to 1 and do not show the large variability of slope b -parameters. Valid ranges are especially important, in case identified prediction equations are applied spatially explicit to areas not monitored. It is important to note that due to the bivariate correlation between slope and runoff ($r = 0.40$ for the total data set) the impact of value changes by one of those predictors on DSI-fluxes cannot be quantified easily. However, because of the design of the prediction equation (Eq. 1), it can be assumed that the combined effect of slope and runoff on DSI-fluxes from each lithological class is appropriately represented for settings of the Japanese Archipelago. This is supported by the significance of the prediction equation ($p < 0.0001$). It is likely that the presented prediction equation does not represent a globally applicable DSI-flux prediction model and further research should try to shed more light on this issue (see Discussion).

Discussion

General discussion

The lumped model approach used here was previously applied on a regional and global scale for other riverine

components than DSi, like suspended matter, alkalinity, organic carbon, nitrogen and phosphorus (Ludwig et al. 1996; Amiotte-Suchet et al. 2003; Bouwman et al. 2005; Seitzinger et al. 2005; Beusen et al. 2005). Results from our study suggest that the multi-lithological lumped model approach is also applicable to predict DSi-fluxes on a regional scale and thus probably on a global scale as well. However, in the latter case, scale issues like for slope or mass transfer processes like uptake of DSi by diatoms in lakes need to be addressed.

For the first time a vector-based lithological map was applied to a multi-lithological approach. In addition, it was aspired not to use a purely statistical approach like multiple linear regression for retrieving a prediction equation (cf. Beusen et al. 2005). Instead, the design of the empirical prediction equation addresses differences in weatherability for each lithological class within each training catchment, hydrological flow processes as well as weathering and transport limitation and is based on previous work on chemical weathering (cf. Bluth and Kump 1994; Gislason et al. 1996; Gaillardet et al. 1999; Moulton et al. 2000; Millot et al. 2002; Lyons et al. 2005). These publications emphasize to isolate the impact of relevant factors on chemical weathering.

Results from here introduced approach supports the hypothesis that functional terms (compare Eqs. 1–3) for each lithological class in prediction equations should not solely be additive, but should be of a multiplicative type for considered relevant predictors. This would allow representing combined influences of first-order controls (like runoff or slope) on DSi-fluxes from the terrestrial to the fluvial system. Additive terms may be appropriate if describing reservoir changes in training catchments, as e.g., plant uptake or lakes.

The overall design of Eq. 1 allows predicting DSi-fluxes for each lithological class in a catchment. Therefore, our approach differs from previous mono-lithological approaches (cf. Bluth and Kump 1994). The general formula identified here can be written for a mono-lithological approach, if applied spatially explicit at the same geodata resolution for slope, as follows:

$$F_i(\text{DSi}) = b_0 s^{b_{s_i}} q^{b_{q_i}} \quad (4)$$

While i represents a lithological class, s slope, q runoff, b_0 , b_{s_i} and b_{q_i} are the estimated b -parameters from Table 2.

Slope was introduced here as a further controlling factor on DSi-fluxes. This decision is supported by research on small Japanese catchments, showing that in steep watersheds event waters and subsurface waters are transported relatively fast to the draining river system, resulting in a relatively short contact time with fresh weatherable rocks or soils if compared to less steep

environments (Sidle et al. 2000; Asano et al. 2003, 2004; Anazawa and Ohmori 2005; Asano and Uchida 2005; Kawai et al. 2006). Observed average slopes suggest that Japanese catchments are in general ‘weathering-limited’ and not ‘transport-limited’ (compare Bluth and Kump 1994; Anderson et al. 2007).

Even though we use only three ‘first-order’ controls (or predictors) on DSi-fluxes (i.e., lithology, runoff and slope) predicted DSi-fluxes correlate highly with measured catchments ($r = 0.885$). Including further factors resulted in a decreasing quality of the prediction model, and may be attributed to the typical settings of the Japanese Archipelago, the used geodata resolution and quality, as well as correlations among analyzed variables. For example, steep areas are dominated by forests and flat areas by agricultural activity or are urban areas. These flat areas are mostly located close to the coast and belong predominantly to lithologies AD or SU (compare Hartmann et al. 2006).

Because the sampling locations were mostly upstream of urban places it is assumed that our results represent DSi-fluxes not significantly impacted by urban areas. The 6.6 times higher than world average specific DSi-fluxes (according to the forced model approach) can be attributed partly to the tectonic setting of Japan as a volcanic island arc adjacent to subduction zones, indicated by spatial earthquake patterns (Dürr et al. 2005, 2008; Hartmann 2005). However, if the approach used here is applied to other regions or on a global scale, resulting b -parameters in the model equation will differ. This can be attributed to the observation that some regions with rather low slope are sometimes characterized by transport limitation instead of weathering limitation with respect to specific DSi-fluxes (cf. Bluth and Kump 1994; Kump et al. 2000). It is likely that further factors like land cover, lake retention or temperature need to be incorporated into a global prediction model. This is because those factors may not correlate significantly with factors applied in this study globally (or regionally), and therefore may partly substitute predictors used here (as, e.g., temperature in this study). In any case correlations among assumed controlling factors have to be analyzed.

The high proportions of volcanics suggest that not only the Japanese Archipelago but the entire “Ring of Fire” around the Pacific could be classified as hyperactive with respect to DSi-flux and silicate weathering. At least for Japan this hypothesis has been tested positively (cf. Dürr et al. 2008).

Discussion of model results

The DSi-flux model used by Bluth and Kump (1994) applied log–log functional relationships between specific

DSi-flux and runoff for five lithological classes (basalt, granite, sandstone, shale and limestone), based on a mono-lithological approach. No differences between consolidated and unconsolidated sediments were made. The effects of other factors on DSi-fluxes were not included.

While using slope as an additional controlling factor, new insights into processes controlling DSi-fluxes on a regional scale are provided. Fluxes decrease with increasing slope for all analyzed lithological classes (Fig. 8), according to the b -parameters retrieved in Eq. 1 (Table 2). The influence of slope is lowest (low to not recognizable) for unconsolidated sediments (AD and SU) and acid plutonics (PA). Due to low values in slope b -parameters (b is close to 0) runoff remains the major important control/predictor on DSi-fluxes for these lithological classes. In contrary, slope may cause variation in specific DSi-fluxes for volcanic lithological classes VB and VA by nearly a factor of 7–10 in case of high runoff ($>1,000 \text{ mm a}^{-1}$) (Figs. 7, 8). Runoff values of more than $1,000 \text{ mm a}^{-1}$ are typical for the Japanese Archipelago (average $1,104 \text{ mm a}^{-1}$). Findings support the hypothesis that under high runoff conditions slope constitutes a stronger controlling factor on specific DSi fluxes than runoff for VA, VB, PY, SS and SM. This highlights the principal importance of uplifting of mountains or tectonic activity for DSi-fluxes.

Even though the influence of temperature and land cover on chemical weathering was identified in general (White et al. 1999; Moulton et al. 2000; Dessert et al. 2003), the incorporation of these factors into the model equation did not improve DSi-flux prediction quality. As discussed above, this may be attributed in part to the observed correlation between the factors slope, runoff, temperature and land cover. This correlation may result into a suppression of their influence in a prediction equation. However, it can not be concluded that these factors do not at all influence specific DSi-fluxes (cf. “Error discussion”). They may be incorporated in future approaches, if reliable functional relations can be identified for representing these factors as controls in a prediction equation. One possibility might be the application of multiple equations for distinguishable regions and recognizing valid ranges of estimated parameters for certain regions, or incorporation of seasonal effects (which were not analyzed here). However, in this case large training data sets are needed to retrieve reliable models. In the context of a prediction model as presented here the term ‘first-order controlling factor’ should be understood as ‘predictor’, because some variables possibly possess prediction potential but are represented in part by others and are thus not considered in the prediction equation.

Error discussion

Lithology

One of the difficulties in applying lumped model approaches is that average catchment characteristics are used for parameter estimation while some lithological classes are characterized by low abundance in training catchments. Because of this, prediction parameters, as for example for lithology SM may not be estimated appropriately. For some classes, like PB or SC no parameters could be identified due to this problem. The natural spatial correlation of some lithological classes, like PY and VB, influences the model outcome as well. In case of low catchment slopes, specific DSi-fluxes from lithological class VB may then exceed those from PY, which is in general not probable due to reasons provided above (cf. Rad et al. 2006). However, the number of catchments used for model development is high if compared to previous approaches, and test statistics support model and estimated parameter validity.

Further uncertainties arise because small scale spatial differences in mineral content of rocks are not covered by the general lithological classification scheme. Due to differences in dissolution kinetics of minerals spatial mineralogical differences may contribute to differences between observed and calculated specific DSi-fluxes.

Runoff

Because of data availability and resolution, runoff remains one of the three factors considered for model calibration which may contribute a significant noise to results. Unfortunately, no monthly runoff data for most of the sampling locations used by Kobayashi were available to calculate monthly fluxes in order to consider seasonality. We used the annual global runoff data set (Fekete et al. 2002) with a resolution of 0.5° that was originally designed to represent global runoff. Thus, runoff may not fully represent local runoff at the time of sampling by Kobayashi. For the few available annual discharge data (Kobayashi 1960) a cross-check was conducted with the runoff data of Fekete et al. (2002). No large differences were observed and it was thus assumed that for this study the applied runoff data are sufficient. So far there are no data to represent differences between rain and snow that could dilute temperature effects or influence weathering rates because of, e.g., differences in soil infiltration or percolation patterns.

Japan has two seasonal precipitation maxima. One occurs during summer (Krishnan and Sugi 2001) in areas facing the Pacific Ocean (southern part of Honshu, Eastern Shikoku and Kyushu). The other occurs during winter in mountainous areas facing the Sea of Japan because air

masses from Central Asia, originally cold and dry, gain water vapor supplied by a warm current intruding the Sea of Japan from the south. Some of this precipitation remains as snow until spring time.

Hydrothermal activity

Influence of hydrothermal activity was minimized by discarding sampling stations with elevated Cl-concentration (see above). Influence of hydrothermal activity on the hydrochemistry of stream and spring water is assumed to be minor for all of Japan, but may be important on a local scale, specifically if seismotectonic processes trigger a substantial fluctuation in water chemistry (Hartmann et al. 2005; Hartmann 2006).

Landcover and vegetation effects

It is known that local DSi cycles are influenced by plant uptake of DSi, transforming DSi into phytoliths (Alexandre et al. 1997; Meunier et al. 1999; Conley 2002). The amount of DSi uptake by plants can be much larger than the mobilization of DSi by weathering (Alexandre et al. 1997; Meunier et al. 1999; Conley 2002) and much of the terrestrial amorphous silica (ASi) in form of phytoliths is recycled. Some of this ASi may be eroded and transported as suspended matter to the coastal zones. Data on ASi transported by rivers in Japan suggest that ASi (terrestrial and fluvial) can be assumed to be in the range of 1/5 to 1/10 of riverine DSi (Isaji 2003; Harashima et al. 2006). However, it can be assumed that the retention of DSi in plants is only relevant for the variability of fluvial DSi-fluxes if the catchment ecosystems are undergoing changes in their biomass (cf. Fulweiler and Nixon 2005), or if a significant change in phytolith dissolution rate occurs.

Furthermore, plants influence weathering processes positively and DSi plant uptake is correlated with available DSi concentration in groundwater and soil solution (Lucas 2001) thus linking it with underlying lithology. Vegetation also influences the water cycle and thus partly controls runoff. Due to these effects land cover is correlated with runoff and lithology (e.g., via relief characteristics induced by underlying lithology and tectonic activity). This correlation and the observation that vegetation distribution is often not correctly displayed by satellite-derived land cover data (Frey and Smith 2007) may make it difficult to improve the used lumped model approach by incorporating land cover as a prediction factor. However, scatter plot analysis revealed at least some relations between land cover and specific DSi-fluxes. For example, catchments characterized by high proportions of forest (>50%) show on average highest

specific DSi-fluxes (Fig. 10). However, due to the other factors influencing DSi-fluxes (Fig. 10) no clear case could be made for including land cover or forest proportion into the model equation. This may be because lithology, slope and runoff represent indirectly some information of land cover effects on DSi-fluxes for Japan. For example, areas dominated by unconsolidated sediments (AD and SU) have high land cover percentages of rice and crop land due to the rather flat slope. In addition, rice terraces and small ponds may be responsible for retention of certain amounts of DSi in form of ASi (cf. Ma et al. 1989; Ma and Takahashi 1989). It is interesting to note, that rice contains 4–20 weight% of SiO₂. However, due to Japan's wet climate it is assumed that some ASi is dissolved rapidly and released as DSi according to the seasonality of harvesting (Ma and Takahashi 1989). Nevertheless, some Si should be removed as ASi by rice harvesting. The tradition of burning rice straw in the original rice paddy field for nutrition after harvesting, may have limited this export. In recent years, this tradition is less and less practiced because of environmental concerns and legislations (personal communications with farmers).

Temperature

A positive correlation between temperature and fluvial DSi-fluxes was identified (Garnier et al. 2006). Such relation could therefore be implemented into the model. In fact, global studies on chemical weathering rates applied temperature as an important factor in models for basalt weathering (Dessert et al. 2003). For a region in the Swiss Alps fluvial silica concentration is correlated with both temperature and elevation (Drever and Zobrist 1992). In case of Japan spatial correlations of temperature with other factors, like climate (precipitation and runoff) and elevation (partly represented by slope) exist. The multiple linear correlation coefficient between temperature, slope and runoff of $r = 0.56$ ($p < 0.0001$) shows that temperature may be partly substituted by annual runoff and slope (Fig. 9). This interpretation is substantiated by the high correlation between observed and predicted specific DSi-fluxes according to Eq. 1 (Fig. 6).

The temperature approach is also hindered by the circumstance that surface air temperature was applied in this study (as well as in previous studies) and that surface temperature may not be representative of temperatures below ground where chemical weathering takes place, e.g., by plant cover influences (compare for further references Anderson et al. 2007). However, temperature effect may have been detected if a larger temperature range would have existed (cf. Dessert et al. 2003).

Anthropogenic effects

The contribution of anthropogenic DSi, specifically in the 1940s and 1950s, when most water samples were taken, is expected to have been very low (Van Dokkum et al. 2004; Garnier et al. 2006). Today, some proportion of DSi can be attributed to detergent use. Since the 1960s an increasing usage of silica containing detergent is noticed in developed countries (Garnier et al. 2006), but anthropogenic contribution to total DSi-fluxes is estimated to be less than 2% (Van Dokkum et al. 2004).

Lake effects

The largest lake in Japan is Lake Biwa, with an area of 670 km², and a catchment of 3,267 km² (according to the digital elevation model). About 70% of the DSi input is retained in the lake (Harashima et al. 2006), reducing the DSi-flux to the Seto Inland Sea by $0.038 \times 10^6 \text{ t SiO}_2 \text{ a}^{-1}$ and total Japanese output by $\sim 0.46\%$ (if compared to the forced model approach fluxes). All lakes and water bodies of Japan amount to 2,375 km², of which Lake Biwa represents 28.2%. Thus, the retention of all lakes (using the lake Biwa estimate) should be $\sim 1.5\%$ for all of Japan.

At the time when Kobayashi conducted his surveys only a few large reservoirs existed in the monitored catchments. The influence of instream diatoms DSi-uptake is probably low because Japanese rivers are short and channel slope is steep. This hypothesis is supported by measurements yielding only low ASi proportions of total Si in Japanese waters (Isaji 2003; Harashima et al. 2006).

Implications for the global carbon cycle

Results indicate that Japan, and probably the entire “Ring of Fire”, are hyperactive with respect to DSi-fluxes. A global estimate of DSi-fluxes to coastal zones supports this interpretation (Dürr et al. 2008). Nevertheless the overall DSi concentration in surface waters of the Pacific is low (Levitus et al. 1993). Both observations support the hypothesis that regions of high tectonic activity may be a factor controlling marine carbon burial rates due to high terrestrial DSi-inputs that stimulate growth of diatoms. Diatom frustules and accompanied particulate organics sink faster to the ocean floor providing less time for remineralisation than organic matter bound to other phytoplankton species, thus leading to higher accumulation and possibly carbon burial rates (Buesseler et al. 2007; Harashima 2007). Thus, the study of regional distribution of DSi-fluxes does not only improve our understanding of the carbon cycle but may also lead to spin-offs regarding

the role of tectonically active times in the geological past and global biogeochemical cycles.

Volcanic areas are important for the carbon cycle also in another aspect: their CO₂ consumption during chemical weathering of silicates (cf. Dessert et al. 2001, 2003; Dupre et al. 2003). Herein it is shown that slope is an important controlling factor for silicate weathering rates. However, steep regions in subtropical or tropical humid climates with high proportions of volcanics are not very well represented in data sets for model calibration in recent global estimates of CO₂-consumption by weathering (cf. Ludwig et al. 1998, 1999; Gaillardet et al. 1999). In addition, the factor slope (relief) is not included in the cited weathering models. Large rivers are often used for model evaluation. However, lithological distribution of 60 large river basins, e.g., applied by Gaillardet et al. (1999), does not differ much from the regions not covered by these large basins (Table 1). Because slope was not subject of previous global weathering studies it can only be speculated if considering its global pattern will influence the estimates of global CO₂-consumption by chemical weathering (currently at 0.25–0.26 Gt C a⁻¹). For further discussion of this issue see Hartmann (2008).

Conclusion

This study presents a new approach for predicting DSi-fluxes on a regional scale that may also be applied on a global scale after modifying the approach. Only three factors are considered in this prediction model because of certain specific conditions of the Japanese Archipelago (i.e., land cover, temperature, soil characteristics, etc.).

Japan constitutes a hyperactive region (10% of its area can even be characterized as hot spot region) with respect to DSi-fluxes, exceeding the global average of DSi-fluxes by a factor of 6.6 (cf. Dürr et al. 2008). Besides runoff, slope constitutes another important factor controlling chemical weathering of silicates and can exceed runoff as first-order control in some cases. Future models may be improved by incorporating mechanistic components such as the lake effect for DSi retention. In addition, the first-order controlling factors applied here (lithology, runoff and slope) can be used in a mechanistic model approach. More research is needed to test and incorporate further factors like temperature, atmospheric deposition, land cover or anthropogenic influences. Applicable functional relationships for prediction equations need to be identified and influences of correlations among predictors have to be addressed. Moreover, to enhance the presented approach, reliable river hydrochemical data are needed for model

calibration and specifically the influence of seasonality should be addressed. Seasonality influence is important in case larger catchments or basins should be recognized in a lumped model approach, because specifically larger river systems are often characterized by strong DSi concentration seasonality, partly controlled by nutrient loads and thus by anthropogenic influence (cf. Hartmann et al. 2007a).

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Appendix A

Distribution of precipitation and atmospheric hydrochemical deposition patterns were calculated from the following references. Based on the regional patterns of both factors silica deposition was interpolated using the product of silica concentration in atmospheric deposition and annual average precipitation.

Anazawa K, Ohmori H (2005) The hydrochemistry of surface waters in andesitic volcanic area, Norikura volcano, central Japan. *Chemosphere* 59:605–615

Anazawa K, Sakamoto H, Tomiyasu T (2007) Influence of ignimbrite on the chemistry of river water in Shirasu plateau, Japan. *Hydrogeol J* 15:409–417

Asano Y, Ohte N, Uchida T (2004) Sources of weathering-derived solutes in two granitic catchments with contrasting forest growth. *Hydrol Process* 18:651–666

Farah A, Rahman A, Hiura H, Shino K (2006) Trends of bulk precipitation and streamwater chemistry in a small mountainous watershed on the Shikoku Island of Japan. *Water Air Soil Pollut* 175:257–273

Fujita S, Takahashi A, Weng JH, Huang LF, Kim HK, Li CK, Huang FTC, Jeng FT (2000) Precipitation chemistry in East Asia. *Atmos Environ* 34:525–537

Fujita SI, Takahashi A, Sakurai T (2003) The wet deposition of acid and some major ions over the Japanese Archipelago. *Tellus Ser B Chem Phys Meteorol* 55:23–34

Fukuzaki N, Oshio T, Noguchi I, Matsumoto M, Morisaki S, Oohara M, Tamaki M, Hiraki T (1999) Spatial

differences of chemical features of atmospheric deposition between rainy season and winter in the areas facing to the Japan Sea, Japan. *Chemosphere* 38:411–423

Hara H (1993) Acid deposition chemistry in Japan. *Bull Inst Public Health* 43:426–437

Hara H (1997) Chemistry of precipitation water in Japan. *Nippon Kagakukaishi* 11:733–748

Kunimatsu T, Hamabata E, Sudo M, Hida Y (2001) Comparison of nutrient budgets between three forested mountain watersheds on granite bedrock. *Water Sci Technol* 44:129–140

Lee BK, Hong SH, Lee DS (2000) Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula. *Atmos Environ* 34:563–575

Nakagawa Y, Iwatsubo G (2000) Water chemistry in a number of mountainous streams of East Asia. *J Hydrol* 240:118–130

Okuda T, Iwase T, Ueda H, Suda Y, Tanaka S, Dokiya Y, Fushimi K, Hosoe M (2005) Long-term trend of chemical constituents in precipitation in Tokyo metropolitan area, Japan, from 1990 to 2002: *Sci Total Environ* 339:127–141

Rasyidin A, Wakatsuki T (1994) Characterization of precipitation and river water chemistry for measuring rates of weathering and soil formation in Iu river watershed, southwestern Japan. *Soil Sci Plant Nutr* 40:319–332

Satake H, Yamane T (1992) Deposition of non-sea salt sulfate observed at Toyama facing the sea of Japan for the period of 1981–1991. *Geochem J* 26:299–305

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Seto S, Hara H, Sato M, Noguchi I, Tonooka Y (2004) Annual and seasonal trends of wet deposition in Japan. *Atmos Environ* 38:3543–3556

Seto S, Nakamura A, Noguchi I, Ohizumi T, Fukuzaki N, Toyama S, Maeda M, Hayashi K, Hara H (2002) Annual and seasonal trends in chemical composition of precipitation in Japan during 1989–1998. *Atmos Environ* 36:3505–3517

Zhang J, Zhang GS, Liu SM (2005) Dissolved silicate in coastal marine rainwaters: comparison between the Yellow Sea and the East China Sea on the impact and potential link with primary production. *J Geophys Res Atmos* 110

Appendix B

Figure 11

Fig. 11 Relationships between specific DSi-fluxes, runoff and slope for catchments dominated (>60% areal proportion) by one lithological class

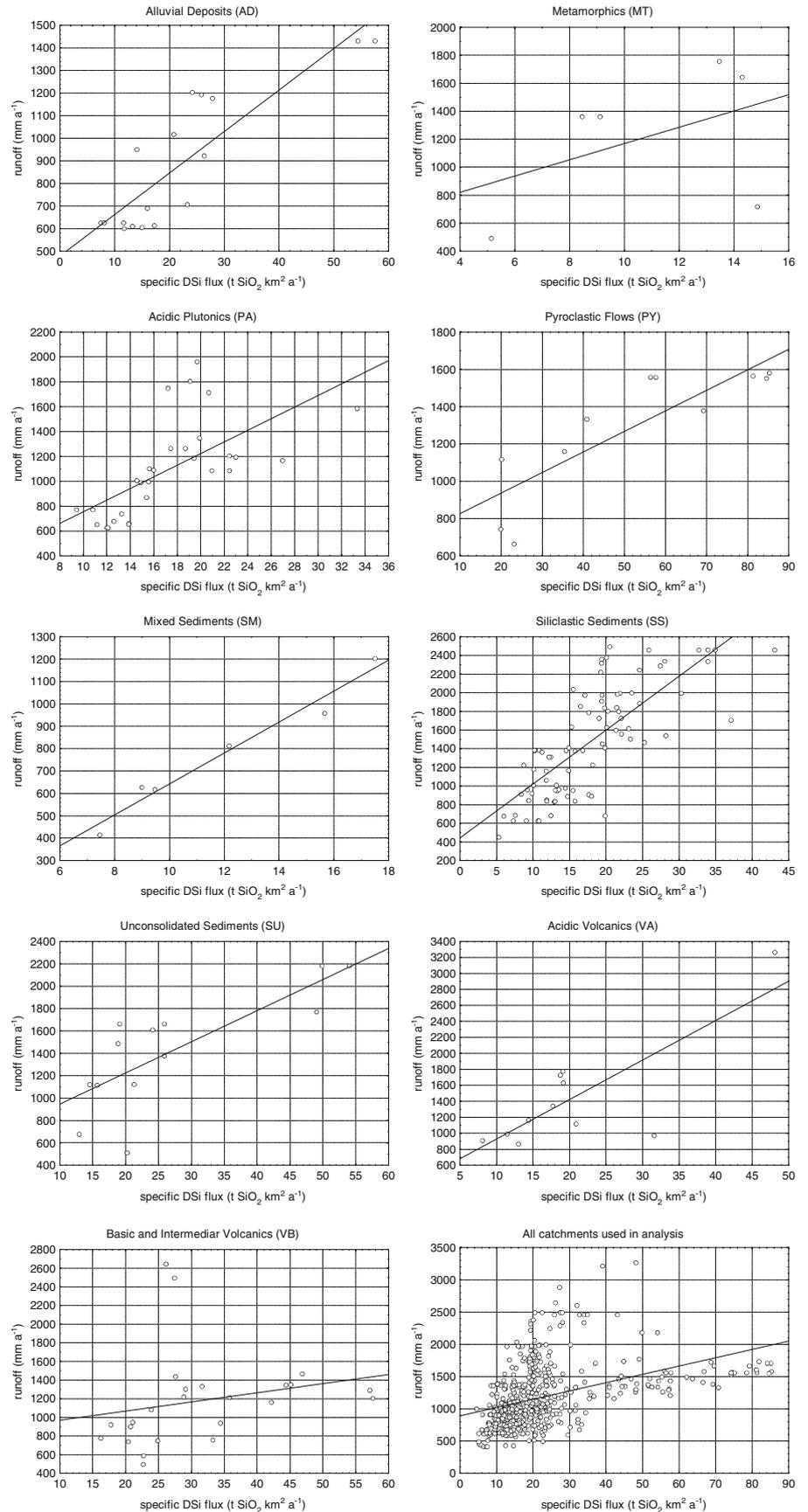
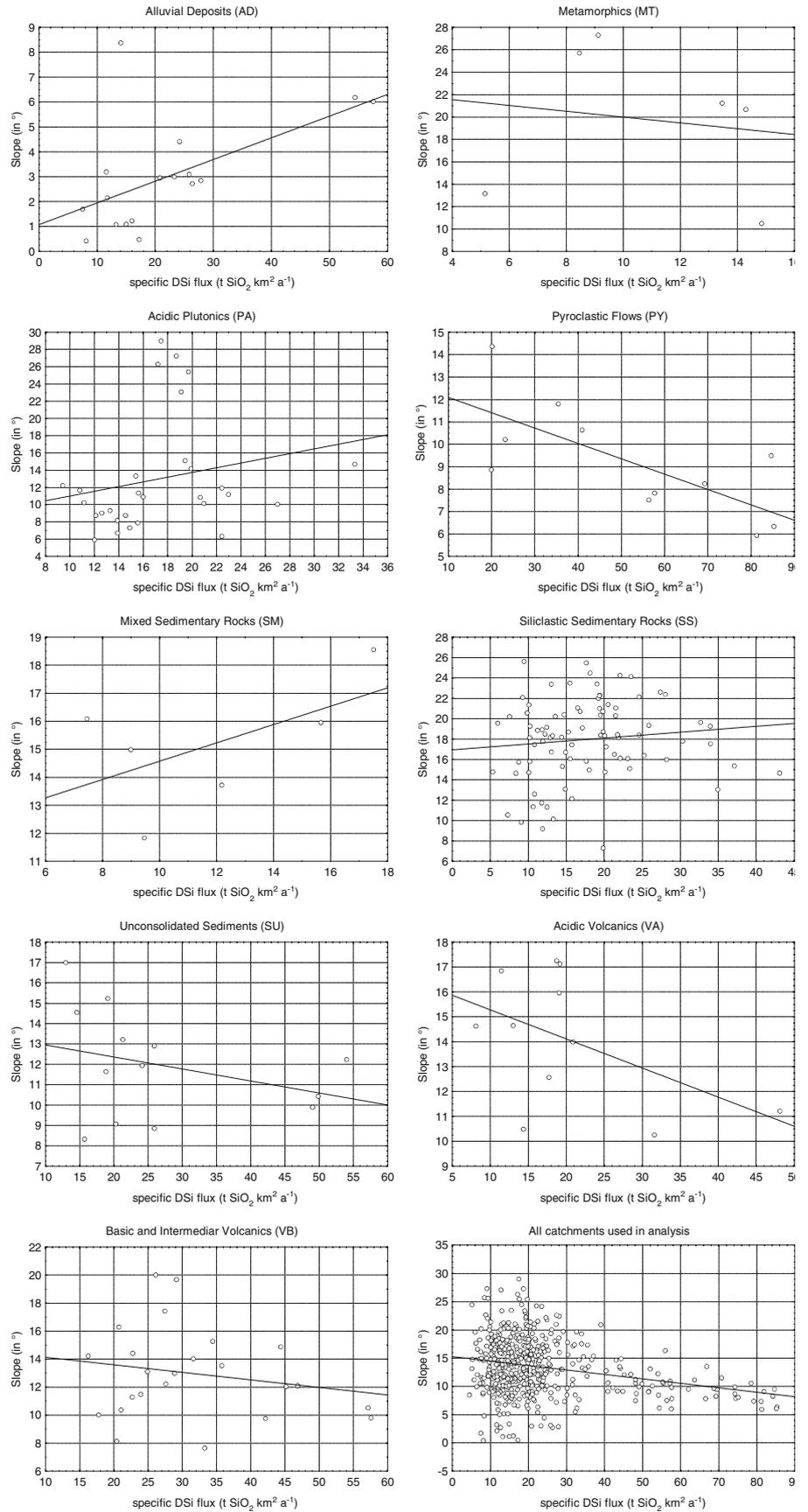


Fig. 11 continued



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