Global importance, patterns, and controls of dissolved silica retention in lakes and reservoirs

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[1] Lentic water bodies (lakes and reservoirs) offer favorable conditions for silica (SiO_2) burial in sediments. Recent global estimates suggest that (1) lentic SiO_2 trapping is a globally important SiO_2 flux, and (2) through reservoir construction, humans have dramatically altered river dissolved SiO_2 (DSi) transport and coastal DSi delivery. However, regional to global scale patterns and controls of DSi removal in lentic systems are poorly constrained. Here we use 27 published lake and reservoir DSi budgets to develop insights into patterns and controls of lentic DSi retention and to develop a new, spatially explicit, global model of lentic DSi removal called SiRReLa (Silica Retention in Reservoirs and Lakes). In our analysis, lentic DSi removal (kg SiO_2 yr^{-1}) was significantly and positively related to DSi loading (P < 0.0001; r^2 = 0.98), and DSi removal efficiency was significantly and positively related to water residence time (P < 0.0001; r^2 = 0.68). In addition, DSi settling rates were, on average, 6.5-fold higher in eutrophic systems than in non-eutrophic systems (median settling velocities: 11.1 and 1.7 m yr^{-1} for eutrophic and non-eutrophic systems, respectively; P < 0.01). SiRReLa, which incorporates these insights, performed quite well in predicting both total DSi removal (kg SiO_2 yr^{-1}; Nash Sutcliffe Efficiency (N.S.E) = 0.88) and DSi removal efficiency (% Si removed; N.S.E. = 0.75), with no detectable bias in the model. Global application of SiRReLa confirms that lentic systems are important sinks for DSi, removing 89.1 Tg DSi yr^{-1} from watersheds globally, roughly 19–38% of all DSi inputs to surface waters. Small lakes and reservoirs (<50 km^2) were critical in the analysis, retaining 81% (72 Tg DSi yr^{-1}) of the globally retained total. Furthermore, although reservoirs occupy just 6% of the global lentic surface area, they retained approximately 35% of the total DSi removed by lentic systems. Regional hot spots for lentic DSi removal were identified and imply that lentic systems can remove the vast majority of DSi across a large fraction of Earth's land surface. Finally, a sensitivity analysis indicates that future improvements in DSi trapping and transport models should focus on improving estimates of DSi input to surface waters.

1. Introduction and Background

[2] Because dissolved silica (SiO_2, hereafter referred to as DSi) is needed in greater quantities by diatoms than by other types of phytoplankton, DSi availability can exert a strong influence on phytoplankton community structure and composition both in freshwaters and the coastal zone [e.g., *Garnier et al.*, 2010; *Tavernini et al.*, 2011]. DSi uptake by phytoplankton can result in the removal of SiO_2 from flowpaths when DSi is incorporated into diatom frustules, sinks to sediments, and is subsequently buried. Recently, several studies have reported a relationship between the occurrence of lakes and Si retention at regional scales [*Conley et al.*, 2000; *Humborg et al.*, 1997, 2000, 2008], and mass balance analyses support that this could be an important phenomenon globally with lakes and reservoirs retaining 13–168 Tg SiO_2 yr^{-1} (0.2–2.8 Tmol yr^{-1}) [*Dürr et al.*, 2011; *Laruelle et al.*, 2009]. Although these estimates are not well-constrained, they imply that DSi storage is a significant flux relative to total coastal DSi delivery (371–462 Tg SiO_2 yr^{-1}; 6.2–7.7 Tmol Si) [*Beusen et al.*, 2009; *Laruelle et al.*, 2009].

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Table 1. List of References, Geographical Locations, and Values of Morphological and Hydrological Variables of Lakes and Reservoirs Used in the Determination of Different Parameter Estimates of the SiRReLa Model

Latitude	Lake or Reservoir Name[a]	Location	Surface Area (km²)	Mean Z (m)	Residence Time (yr)	% DSi Removal	V_f	H_1 (m yr⁻¹)	Trophic Status	Reference[b]
59.5	Malaren	Sweden	1140	13	3.00	51.16	3.11	4.33	mesotrophic	1
59	Vanern	Sweden	5650	27	9.00	35.71	1.33	3.00	mesotrophic	1
58.5	Vattern	Sweden	1900	40	58.00	76.09	0.99	0.69	oligotrophic	1
−12.2	Malawi	Malawi	29600	292	140.00	96.36	6.91	2.09	mesotrophic	2
44	Michigan	United States	58000	84	100.00	82.19	1.45	0.84	oligotrophic	3
43.6	Mirror	United States	0.15	5.75	1.02	55.86	4.61	5.64	oligotrophic	4
68.6	Toolik Lake	United States, AK	1.5	7	1.00	17.06	1.31	7.00	oligotrophic	5
63.6	P&N	Hudson's Bay	0.0709	3.28	2.90	73.00	1.48	1.13	oligotrophic	6
63.6	Far	Hudson's Bay	0.037	3.61	2.93	80.00	1.99	1.23	oligotrophic	6
63.6	Spring	Hudson's Bay	0.0693	2.71	1.63	57.00	1.40	1.66	oligotrophic	6
63.6	Jade	Hudson's Bay	0.0363	1.82	0.85	90.00	4.93	2.14	oligotrophic	6
56.2	Loch Leven	Scotland	13.31	3.9	0.40	70.41	11.87	9.75	eutrophic	7, 8
44.9	St. Croix*	United States	35	14	0.10	3.77	146.00	146.00	eutrophic	9
44.4	Pepin*	United States	103	8.9	0.05	−10.80	−17.53	170.97	mesotrophic	9
44.4	Iron Gate*	Romania	156.4	17.26	0.03	4.00	25.72	629.99	eutrophic	10
49.2	Solina-Myczowce*	Poland	24	22	0.61	20.00	8.11	36.33	oligotrophic	11
048.3	Marne*	France	48	7.2	0.46	47.00	9.94	15.65	eutrophic	12
48.2	Seine*	France	23	7.6	0.62	57.00	10.35	12.26	eutrophic	12
48.2	Aube*	France	21	8.9	0.40	43.00	12.51	22.25	eutrophic	12
48.2	Amance*	France	0.5	4.5	0.03	9.30	16.89	173.08	eutrophic	12
48.3	Champaubert*	France	0.5	3.5	0.11	15.50	5.36	31.82	eutrophic	12
46	Lake Lugano	Switzerland/Italy	27.5	171	180.40	78.40	1.45	0.95	eutrophic	13
35.2	Lake Biwa	Japan	670	41	5.00	77.78	12.33	8.20	eutrophic	14
−35.5	Lake Alexandrina*	Australia	580.6	2.86	0.30	39.00	4.73	9.58	mesotrophic	15, 16
27	Dongfeng*	China	19.7	52.0	0.1	−5.46	−27.66	520.30	oligotrophic	17
27	Suofengying*	China	5.7	23.5	0.016	−7.3	−103.52	1469.29	mesotrophic	17
−35.5	Wujiangdu*	China	47.5	48.4	0.14	22.8	89.50	345.86	eutrophic	17

[a]Asterisk indicates system is a man-made reservoir.
[b]References: (1) *Conley et al.* [2000], (2) *Hecky et al.* [1996], (3) *Schelske* [1985], (4) *Likens* [1985], (5) *Cornwell and Banahan* [1992], (6) *Welch and Legault* [1986], (7) *Bailey-Watts et al.* [1989], (8) *Smith* [1974], (9) *Triplett et al.* [2008], (10) *Teodoru and Wehrli* [2005], (11) *Koszelnik and Tomaszek* [2008], (12) *Garnier et al.* [1999], (13) *Hofmann et al.* [2002], (14) *Goto et al.* [2007], (15) *Cook et al.* [2010], (16) *Geddes* [1984], (17) *Wang et al.* [2010].

[3] To our knowledge, a generalized model relating lake and reservoir characteristics to DSi retention efficiency has not previously been developed or published. In a recent analysis, *Beusen et al.* [2009] used relationships developed for total suspended solid burial and total phosphorus burial to estimate DSi burial in large reservoirs at the large river basin scale. However, they acknowledged significant uncertainty in their estimate due to the lack of a DSi-specific model for DSi retention and called for the development of such a model. In addition to lending insight into spatial patterns and magnitudes of DSi retention, a predictive model for DSi retention, when used in conjunction with other nutrient loading and retention models, could indicate where, globally, diatom-dominated primary production is and is not likely.

[4] Here we use 27 published lake and reservoir DSi budgets to characterize lentic Si retention dynamics and use this information to develop a global scale model capable of resolving regional differences in lentic DSi removal called the Silica Retention in Reservoirs and Lakes (SiRReLa) model. We then apply this new, spatially explicit, half-degree resolution, annual-scale, global model of DSi removal in lakes and reservoirs to evaluate the relative importance of lake and reservoir systems as sinks for DSi, and to gain insight into where DSi is likely to be abundant and where it is likely to be in short supply. Finally, the SiRReLa model is subjected to a sensitivity analysis, and results of this analysis are used to suggest ways to enhance

future iterations of the SiRReLa model and other, similar models.

2. Methods

2.1. SiRReLa Model Development, Structure and Calibration

[5] To determine which factors exert important controls on DSi retention in lakes and reservoirs across large spatial scales, peer-reviewed studies were mined for information on DSi retention and system characteristics likely to co-vary with or control DSi retention and DSi retention efficiency. In all, 27 lentic systems (15 lakes and 12 reservoirs) with sufficient data to support the testing and development of a DSi retention model were identified and collated into a data set that includes lakes from a broad range of size classes, regions, and land-use intensities (Table 1). To avoid the potentially confounding influence of seasonal Si uptake and storage, lakes and reservoirs were included in our analysis only if at least one complete year of data during the ice-free period was available.

[6] The fraction of DSi that enters lakes and reservoirs and does not leave as DSi (R_{cal}; unit-less) was estimated as:

$$R_{cal} = \frac{Si_{in} - Si_{out}}{Si_{in}} \quad (1)$$

where Si_{in} is the mass or average concentration of DSi estimated to enter a lake or reservoir annually (kg SiO₂ yr⁻¹)

and Si_{out} is the mass of DSi (kg SiO$_2$ yr^{-1}) or average concentration estimated to exit a lake or reservoir annually via surface water outlet(s). As defined above, R_{cal} includes both DSi that is taken up by diatoms and subsequently buried in sediments and DSi that is transformed into biogenic silica (BSi) and transported downstream. Throughout, masses refer SiO$_2$, not elemental Si.

[7]   For each lake and reservoir in our calibration data set, an apparent settling velocity for DSi ($V_{f\text{-}cal}$) and hydraulic load ($H_{l\text{-}cal}$) were estimated. V_f is essentially a piston velocity for DSi removal in lentic systems and accounts for Si removed via burial in sediments. V_f in SiRReLa differs from V_f often used to describe aquatic N uptake and removal. Whereas V_f used in lentic N removal models is affected by both rates of N burial in sediments and denitrification rates [*Harrison et al.*, 2009], V_f in SiRReLa only describes the rate of Si burial following biotic uptake. Hydraulic load ($H_{l\text{-}cal}$) was estimated as:

$$H_{l-cal} = \frac{z}{T} \qquad (2)$$

where z is lake or reservoir average depth (m) and T is water residence time (yr: calculated as lake volume/water discharge). $V_{f\text{-}cal}$ was estimated as:

$$V_{f-cal} = -H_{l-cal} \times \ln(1 - R_{cal}) \qquad (3)$$

where $H_{l\text{-}cal}$ is hydraulic load and $R_{\text{-}cal}$ is a measurement-based estimate of the fraction of DSi entering lakes and reservoirs that is either retained or transformed into BSi (equation (1)).

[8]   Ancillary information was also collected for each system, including name, location (approximate latitude and longitude), system type (lake or reservoir), system trophic status, water inflow, mean depth, system surface area, and system watershed area (Table 1). In the SiRReLa model development process, we tested for significant empirical relationships between DSi retention and potential controlling variables using simple and multiple regression approaches. We also tested for significant differences ($p < 0.05$) in average apparent settling velocity (V_f) among different categories of lakes and reservoirs using one-way ANOVAs. In order to satisfy the assumptions of equal variances and normal distribution of the residuals of the ANOVA test, variables were transformed as necessary. Three reservoirs from a single study (Dongfeng, Suofengying, and Wujiangdu) [*Wang et al.*, 2010] were excluded from this analysis due to anomalous (>1 SD from the mean) V_f values (Table 1). However, these systems were included during the model testing process.

2.2.   Model Structure

[9]   Based on analysis described in section 3.1, the SiRReLa model was formulated to estimate annual lentic DSi removal globally, in a spatially distributed fashion. In the SiRReLa model, DSi removal (Si_{rem}; kg SiO$_2$ yr^{-1}) for lakes and reservoirs is calculated as:

$$Si_{rem} = R \times Si_{in} \qquad (4)$$

where Si_{in} is an estimate of DSi input to lake and reservoir surface waters, from *Beusen et al.* [2009], and R is an

estimate of the fraction of DSi retained within lakes and reservoirs. R is calculated as:

$$R = 1 - \exp\frac{-V_f}{H_l} \qquad (5)$$

where V_f is the apparent settling velocity (also occasionally referred to as an apparent nutrient uptake velocity [e.g., *Wollheim et al.*, 2008]) for DSi (m yr^{-1}) by lake or reservoir sediments, and H_l is the hydraulic load (m yr^{-1}) for a given lake, reservoir, or a series of tightly coupled reservoirs. This formulation has been used successfully to estimate N retention by lakes and reservoirs [*Wollheim et al.*, 2006; *Alexander et al.*, 2002; *Harrison et al.*, 2009]. Theory predicts that if H_l is much greater than V_f for a given lentic system, retention efficiency of that system will be low because water flux will outstrip the system's capacity to process DSi. Conversely, if H_l is much lower than V_f, DSi retention efficiency should be high. H_l (m yr^{-1}) was calculated as:

$$H_l = \frac{1000 \times Q}{A} \qquad (6)$$

where Q is water input to lakes and reservoirs (km^3 yr^{-1}) and A (km^2) is either surface area of individual lakes (for large lake analysis) or cumulative surface area of lakes in a given half-degree grid cell (for small lake analysis). H_l can be calculated either according to equation (2) or equation (6).

[10]   Although several aspects of the SiRReLa model are similar to a model previously developed to estimate nitrogen retention by reservoirs and lakes called NiRReLa [*Harrison et al.*, 2009], SiRReLa differs from NiRReLa in important respects. While both models predict nutrient retention as a function of nutrient input, H_l, and apparent settling velocity (V_f), both the magnitudes of V_f and the factors controlling V_f differ substantially between the two models. In NiRReLa V_f varies depending upon whether a system is a lake or a reservoir [*Harrison et al.*, 2009]. For SiRReLa, separate V_f values were assigned for eutrophic and non-eutrophic systems, calculated as the median V_f of eutrophic and non-eutrophic calibration systems, respectively. The threshold between non-eutrophic and eutrophic systems was set at 10 kg DIP-P km^{-2} yr^{-1} because this threshold maximized correspondence between eutrophication status as reported for lakes and reservoirs in the SiRReLa calibration data set and eutrophication status as predicted by NEWS-DIP-HD [*Harrison et al.*, 2010].

2.3.   Global Application of SiRReLa
2.3.1.   Spatial Data

[11]   Spatial data sets used in the global application of the SiRReLa model all had a spatial resolution of 0.5° × 0.5° (approximately 50 km × 50 km at the equator) and were selected to represent modern (year 2000) conditions. Water runoff (m yr^{-1}), water discharge (km^3 yr^{-1}), and basin delineations for large rivers were taken from *Fekete et al.* [1999]. Estimates of DSi loading to surface waters were estimated using pre-dam-processing output of the Nutrient Export from Watersheds–Dissolved Silica (NEWS-DSi) model [*Beusen et al.*, 2009]. *Beusen et al.* [2009] estimate DSi inputs to surface waters at the scale of large watersheds

as a function of precipitation, lithology, soil bulk density and watershed slope. Lake locations and attributes were taken from *Lehner and Döll* [2004], currently the most comprehensive, global survey of lentic water bodies, containing 243,071 lakes and 822 reservoirs.

[12] For the global application of SiRReLa, lake trophic status was estimated at a half degree resolution using a model of dissolved inorganic phosphorus (DIP) loading (NEWS-DIP-HD) [*Harrison et al.*, 2010]. Based on an analysis that maximized correspondence between NEWS-DIP-HD predictions and reported trophic status of lakes and reservoirs in the calibration data set, a threshold of 10 kg DIP-P km^{-2} yr^{-1} was used to categorize lakes and reservoirs as either eutrophic or non-eutrophic, and V_f values were assigned accordingly. DIP rather than another element or element form was chosen as an indicator of trophic status because P is often the limiting nutrient in lentic systems [*Schindler et al.*, 2008; *Sterner*, 2008] and because DIP is the most readily bioavailable form of P. This approach categorized 74% of the calibration lakes and reservoirs correctly. The potential effects of possible incorrect categorization of lake and reservoir trophic status are explored via a sensitivity analysis (described below in section 3.5).

[13] In order to accommodate differences in data availability between large and small lakes for model calculations, lakes were divided into two size classes (large and small) where lakes and reservoirs with surface areas greater than 50 km^2 are referred to as "large" and those between 0.001 and 50 km^2 are referred to as "small." One-tenth of a hectare (0.001 km^2) was considered to be the smallest surface area for a perennial water body, as in *Downing et al.* [2006]. Distribution of small lakes is described below.

2.3.2. SiRReLa and Small Lakes and Reservoirs (<50 km^2)

[14] Small lakes and reservoirs are extremely numerous and constitute a significant portion of the total surface area of lakes and reservoirs globally (approximately 31% for lakes <0.1 km^2 according to *Downing et al.* [2006] and roughly 4% of total reservoir area according to *Lehner et al.* [2011]. Small lentic systems are important sites for biogeochemical processing [*Wetzel*, 2001; *Downing*, 2010], and, as such, we deemed it important to include these small systems in SiRReLa. However, this presented a challenge, as there is currently no global database that includes anywhere near all water bodies smaller than 0.1 km^2. To overcome this limitation in the available global data, we assumed that the spatial distribution of the smallest lakes (<0.1 km^2) would scale in a linear fashion with the distribution of slightly larger (0.1–50 km^2) lakes. Lakes and reservoirs were assumed to have a Pareto-type size distribution, as demonstrated by *Downing et al.* [2006], and the shape of this distribution was determined by a coefficient c, describing the relative abundance of large versus small lakes. We then calculated the total global number and surface area of small lakes and reservoirs. The number, average surface area, and cumulative surface area of lakes and reservoirs within given size ranges were determined as in *Downing et al.* [2006], using identical coefficients.

[15] Total global small lake and reservoir surface areas were then distributed on the global landscape. Small lake surface areas (A_{sm}) were distributed in direct proportion to

the distribution of smaller lakes (0.1–50 km^2) in the *Lehner and Döll* [2004] database as:

$$A_{sm} = A_{sm-tot} \frac{A_{GLWD2-cell}}{A_{GLWD2-tot}} \tag{7}$$

where A_{sm} is the total surface area of lakes 0.001–50 km^2 in each cell, A_{sm-tot} is the calculated global total surface area of lakes with individual surface areas between 0.001 and 50 km^2, $A_{GLWD2-cell}$ is the lake surface area of 0.1–50 km^2 lakes in a given cell as reported in *Lehner and Döll* [2004], and $A_{GLWD2-tot}$ is the global total lake surface area of 0.1–50 km^2 lakes as reported in *Lehner and Döll* [2004]. Due to a general lack of data on global spatial distribution of small reservoirs, these systems were distributed uniformly across all grid cells between 55°N and 55°S. A$_{sm-tot}$ was 2.55×10^6 km^2 for lakes and 9.83×10^4 km^2 for reservoirs. For comparison, the total small lake and reservoir surface area values in *Lehner and Döll* [2004] were 3.7×10^5 and 2.8×10^3, respectively, highlighting the importance of including the smallest lakes and reservoirs. In a more recent, more complete, analysis of global reservoirs, total surface area of all reservoirs smaller than 10 km^2 was 6.8×10^4 km^2 [*Lehner et al.*, 2011], in general agreement with our estimate.

[16] The fraction of DSi removed by small lakes and reservoirs (R_{sm}) was calculated as in equation (5) [see *Wollheim et al.*, 2006; *Alexander et al.*, 2002], and DSi removal in small lakes and reservoirs was calculated as the product of R and DSi load. Hydraulic load for small lakes and reservoirs (H_{l-sm}) was calculated as in equation (6). For small lakes and reservoirs, Q is total discharge (km^3 yr^{-1}) generated within each half-degree cell and A is the cumulative surface area of small (<50 km^2) lakes or reservoirs in a given half-degree cell.

2.3.3. SiRReLa and Large Lakes and Reservoirs (>50 km^2)

[17] The spatial distribution of large lakes and reservoirs was taken from the global database of *Lehner and Döll* [2004], which contains 3067 of the largest lakes (area ≥50 km^2) and 654 of the largest reservoirs globally (storage capacity ≥0.5 km^3). Lakes and reservoirs in *Lehner and Döll* [2004] <50 km^2 are accounted for above.

[18] We estimated annual DSi removal (kg Si yr^{-1}) in these large lakes and reservoirs (Si_{large}) according to equations (4) and (5), just as for small lakes and reservoirs. However, Si_{in} and H_l are calculated somewhat differently for large lakes than for small lakes. For large lakes and reservoirs Si_{in}, the amount of DSi estimated to enter a given large lake or reservoir annually, is calculated as:

$$Si_{in} = W \times Si_{surf} \tag{8}$$

where W represents the surface area of the land contributing runoff to a given large lake or reservoir (km^2) and Si_{surf} is the area-weighted average rate of DSi yield to surface waters (kg Si km^{-2} yr^{-1}) within the large river watershed [*Fekete et al.*, 1999] in which a large lake or reservoir is located, as estimated by *Beusen et al.* [2009]. Hydraulic load for large lakes and reservoirs (H_l) was calculated according to equation (6). Rather than being estimated at the grid-cell level as for small lakes and reservoirs, values for Q and A for

Table 2. Comparison of Average Apparent Settling Velocities for DSi (V_f) Among Different System Classifications[a]

Axis of Comparison	Systems Compared	n	V_f (m y^{-1})	SD
Overall mean		24	5.7	7.8
Trophic Status	Eutrophic	10	11.2*	6.7
	Non-eutrophic	14	1.8*	6.1
System type	Lakes	15	4.0	3.7
	Reservoirs	9	8.6	11.6
Surface Area	>50 km^2	9	4.3	11.4
	<50 km^2	15	6.5	4.9
Latitude	Boreal	9	3.2	3.5
	Temperate	14	7.2	9.6
	Tropical	1	6.9	N/A

[a]Asterisk denotes a significant difference among systems via 1-way ANOVA. All other comparisons were not statistically significantly different (P > 0.05). Three reservoir systems with V_f values falling beyond one standard deviation (28.6 m y^{-1}) from the whole data set average (3.5 m y^{-1}) were excluded from this analysis.

large systems were taken directly from *Lehner and Döll* [2004]. To avoid double counting DSi removal by both large and small lakes, we assumed that small lakes and reservoirs "see" (and can retain) DSi before it reaches large lakes or reservoirs.

2.4. Model Sensitivity Analysis

[19] A sensitivity analysis was performed in order to evaluate the response of SiRReLa model output to changes in various input parameters, including: rates of water runoff and DSi loading, the number, size and spatial distribution of lakes and reservoirs, system trophic status, and V_f within lakes and reservoirs. Water runoff and Si loading were both halved and doubled. Trophic status was set to both all eutrophic and all non-eutrophic.

[20] We also evaluated the SiRReLa model's sensitivity to the number, size and spatial distribution of lakes and reservoirs in several ways. First, we ran SiRReLa without any extrapolation to include the world's smallest lakes, including only lakes and reservoirs reported in a spatially explicit global data set of small (0.1–50 km^2) lakes and reservoirs [*Lehner and Döll*, 2004]. In a second approach, we only extrapolated down to lakes with a surface area≥0.01 km^2. In an additional experiment, we further tested SiRReLa's sensitivity to changes in the number of small lakes and the shape of the Pareto distribution [cf. *Seekell and Pace*, 2011] by varying the Pareto exponent (c in equations 4, 5, and 10 in *Downing et al.* [2006]) by ±1 S.E. Finally, sensitivity of SiRReLa predictions to changes in V_f was also evaluated by varying V_f from the 25th percentile value to the 75th percentile of all non-eutrophic and eutrophic systems in our calibration data set.

3. Results and Discussion

3.1. System Characteristics and DSi Trapping Efficiency

[21] In order to develop an effective DSi trapping model, it was necessary to first understand interactions between lake and reservoir characteristics and DSi trapping efficiency. To gain this understanding, we tested for significant relationships between DSi removal and characteristics of lentic systems that had the potential to covary with or control DSi

retention. We observed strong positive, linear relationships between DSi loading and DSi removal (p < 0.0001; r^2 = 0.98), between water residence time and DSi retention efficiency (p < 0.0001, R^2 = 0.68), and between log-transformed hydraulic load and DSi export efficiency (p < 0.0001, R^2 = 0.77). Best fit regression models for these relationships were as follows:

$$\log_{10}Si_{Rem} = 1.01 \times \log_{10}Si_{in} - 0.46 \qquad (9)$$

$$R_{cal\_pct} = 23.79 \times \log_{10}T + 43.50 \qquad (10)$$

$$R_{cal\_pct} = 29.06 \times \log_{10}H_l + 23.92 \qquad (11)$$

where R_{cal_pct} is R_{cal} multiplied by 100, and other symbols are as previously defined.

[22] In addition, V_f was significantly higher (p < 0.01by 1-Way ANOVA; Table 2) in eutrophic lakes and reservoirs (mean: V_f: 11.2 m yr^{-1}; median: V_f: 11.1 m yr^{-1}) than in oligotrophic and mesotrophic lakes and reservoirs (mean: V_f: 1.8 m yr^{-1}; median: V_f: 1.7 m yr^{-1}). Assigning 10 kg km^{-2} yr^{-1} as a threshold between eutrophic and non-eutrophic conditions, the NEWS-DIP-HD model predicted trophic status correctly for 74% of the lentic systems in the calibration data set. Higher and lower DIP yield thresholds resulted in decreased accuracy in assigning lentic system trophic status. When assignment of trophic status was incorrect (26% of cases), this method incorrectly assigned eutrophic status to non-eutrophic systems more frequently than the reverse (6 cases and 1 case, respectively). Median V_f values assigned to eutrophic and non-eutrophic systems using this approach (1.7 m yr^{-1} and 11.1 m yr^{-1}, respectively) were incorporated into the SiRReLa model. A strong positive relationship (p < 0.0001, R^2 = 0.72) was also observed between NEWS-DSi-predicted DSi loading and DSi loading either reported for individual systems or calculated from information provided by individual studies (Figure 3).

[23] No other significant relationships between potential controlling variables and DSi retention or DSi retention efficiency were observed. V_f was not significantly different in oligotrophic lakes than in mesotrophic lakes or between lakes and reservoirs (P ≫ 0.05 in both cases). No significant relationship was observed between DSi retention efficiency and absolute value of latitude. There was also no significant relationship between SiRReLa model error (predicted minus observed DSi retention efficiency) and the absolute value of latitude; nor was there any statistically significant correlation between V_f and system size.

3.2. SiRReLa Model Performance

[24] It was not feasible to directly test the results predicted by the entire SiRReLa model (i.e., regional and global scale predictions) because there currently is no appropriate global- or large regional-scale validation data. However, we were able to evaluate the SiRReLa model's capacity to predict percent DSi retention and total DSi retention within individual lakes and reservoirs by comparing measurement-based estimates of DSi removal in lakes and reservoirs (equation (1)) with SiRReLa-modeled estimates of DSi removal (equation (5)). In these tests, the SiRReLa model performed quite well (Figures 1 and 2). Nash-Sutcliffe
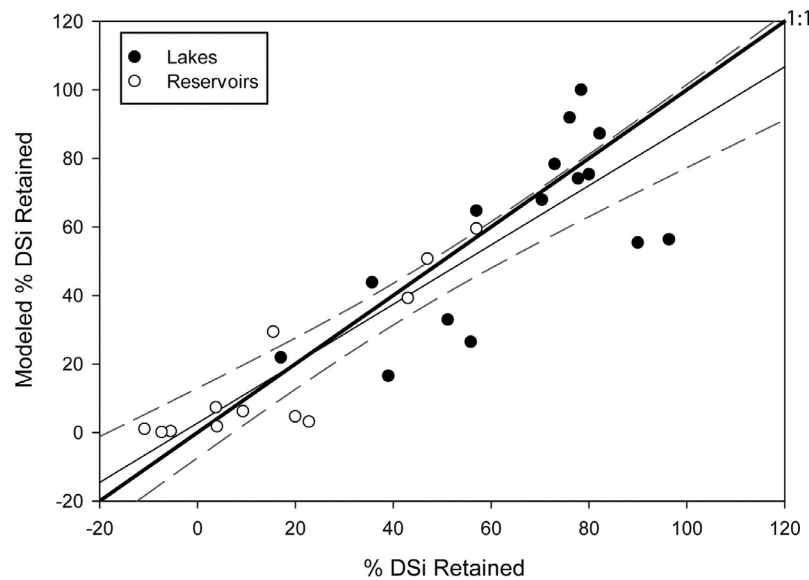
Figure 1. Comparison between measured percent DSi removal and SiRReLa-modeled percent DSi removal in lakes (filled circles) and reservoirs (open circles). The 1:1 line (bold), OLS regression line (thin black line), and 95% confidence intervals (dotted lines) are shown.

efficiency of a comparison between model-predicted DSi retention efficiency and measured DSi retention efficiency was 0.80 for lakes and reservoirs together and 0.79 for reservoirs alone (Figure 1). The root mean squared error for the SiRReLa model was 10.1% for both lakes and reservoirs, and 75% and 95% of the predictions fell within 16% and 30% of the measured removal rates, respectively. The least squares regression between measured and modeled DSi removal efficiency was not significantly different from unity (Figure 1), indicating a lack of systematic bias.

[25] A similar analysis was conducted for total DSi retention. This analysis yielded Nash-Sutcliffe efficiencies of 0.96, 0.51, and 0.88 for comparisons between log-transformed predicted and log-transformed measured DSi retention for lakes, reservoirs, and the entire lentic system data set, respectively. As with the DSi removal efficiency, there was no detectable bias in the model based on a comparison of the least squares regression and the 1:1 line. Hence, it was possible to use the SiRReLa model to develop half-degree, global estimates of lake and reservoir DSi removal efficiency and DSi removal rate.
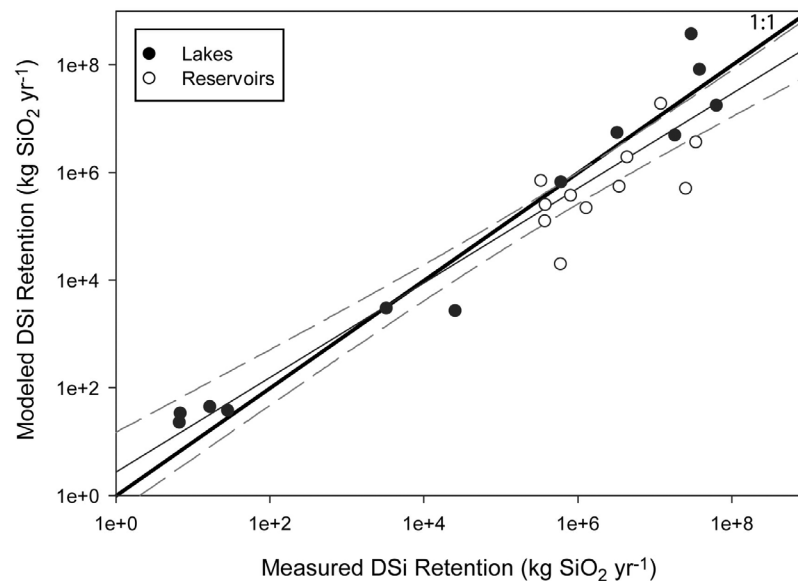

Figure 2. Comparison between measured total DSi removal (kg SiO_2 yr^{-1}) and SiRReLa-modeled DSi removal (kg SiO_2 yr^{-1}) for lakes (filled circles) and reservoirs (open circles). The 1:1 line (bold), OLS regression line (thin black line), and 95% confidence intervals (dashed lines) are shown.

Table 3. Global Scale SiRReLa DSi Removal Estimates for Different Aquatic System Classes[a]

Waterbody Type	Surface Area (km^2)	DSi Retained Globally (Tg SiO$_2$ yr^{-1})	DSi Retained per Unit Area (g SiO$_2$ m^{-2} yr^{-1})
Small Lakes	1.9×10^6	46.9	18.0
Large Lakes	1.2×10^6	11.2	9.3
All Lakes	3.1×10^6	58.1	15.3
Small Reservoirs	8.0×10^4	24.9	311.3
Large Reservoirs	1.5×10^5	6.1	40.7
All Reservoirs	2.3×10^5	31.0	124.0
Reservoirs and Lakes Combined	3.3×10^6	89.1	21.7

[a]Surface area represents the global surface as estimated by SiRReLa for small lakes and reservoirs (0.001–50 km^2) and large lakes and reservoirs (>50 km^2).

3.3. DSi Removal by Lakes and Reservoirs at Global Scale

[26] Using the SiRReLa model, we estimate that, globally, lentic aquatic systems larger than 0.001 km^2 remove 89.1 Tg SiO$_2$ yr^{-1} (1.5 Tmol Si yr^{-1}) from watershed flow paths (Table 3). This is equivalent to 19–39% of the 227–466 Tg Si yr^{-1} estimated to enter surface freshwaters globally [Beusen et al., 2009; Dürr et al., 2011; Laruelle et al., 2009] and falls within the range of recent estimates of global lentic DSi retention (47–168 Tg SiO$_2$ yr^{-1}) [Beusen et al., 2009; Laruelle et al., 2009; Dürr et al., 2011]. SiRReLa attributes 31.0 Tg SiO$_2$ yr^{-1} of DSi removal to trapping behind dams, an estimate that falls within the range of recent estimates of reservoir DSi trapping (13.2–39.6 Tg SiO$_2$ y^{-1}) [Beusen et al., 2009; Dürr et al., 2011].

[27] Using SiRReLa we estimate that the average area-specific rate of DSi removal by lentic systems globally is 21.7 g SiO$_2$ m^{-2} yr^{-1} (Table 3), well within—although toward the low end of—measured per-area DSi retention rates for individual lakes in this study (-164.4–219.3 g Si m^{-2} yr^{-1}) and within the range of measured sediment BSi accumulation rates globally (0.2–1,497.4 g SiO$_2$ m^{-2} yr^{-1}). It is also consistent with a prior estimate of DSi retention in lakes, floodplains, and reservoirs by Campy and Meybeck [1995], who reported a "crude estimate" of global retention by these systems of 20 ± 10 g SiO$_2$ m^{-2} y^{-1}, based on a few lakes. We were initially concerned that using NEWS-DSi model output as DSi input to the SiRReLa model would result in a significant underestimate of lake and reservoir DSi retention. This is because NEWS-DSi was calibrated against coastal DSi delivery (without reservoir DSi removal), and may therefore significantly underestimate the amount of DSi mobilized from the regolith. For example, in an independent derivation from first principles, Hilley and Porder [2008] estimate that 1,142–2,764 Tg SiO$_2$ y^{-1} are weathered from rocks and soils globally. This estimate is much larger than that of NEWS-DSi (380 Tg SiO$_2$ yr^{-1}), and if most of this weathered DSi enters surface waters, then SiRReLa, as currently formulated, would dramatically underestimate lentic DSi trapping. However, a comparison between measured and NEWS-DSi-modeled DSi loading to individual lakes and reservoirs suggest that NEWS-DSi predictions to lakes and reservoirs are not subject to systematic over- or under-prediction (Figure 3).

[28] Results from SiRReLa suggest that small lakes and reservoirs play a crucial role in the global DSi cycle as sites where significant DSi removal from flowpaths occurs. SiRReLa model output indicates that small lakes remove more than four times as much DSi from watersheds as large lakes (46.9 Tg SiO$_2$ yr^{-1} for small lakes versus 11.2 Tg SiO$_2$ yr^{-1} for large lakes), and that small lakes (<50 km^2) account for over half of the 89.1 Tg SiO$_2$ yr^{-1} removed by lentic systems (lakes and reservoirs combined) globally (Table 3).
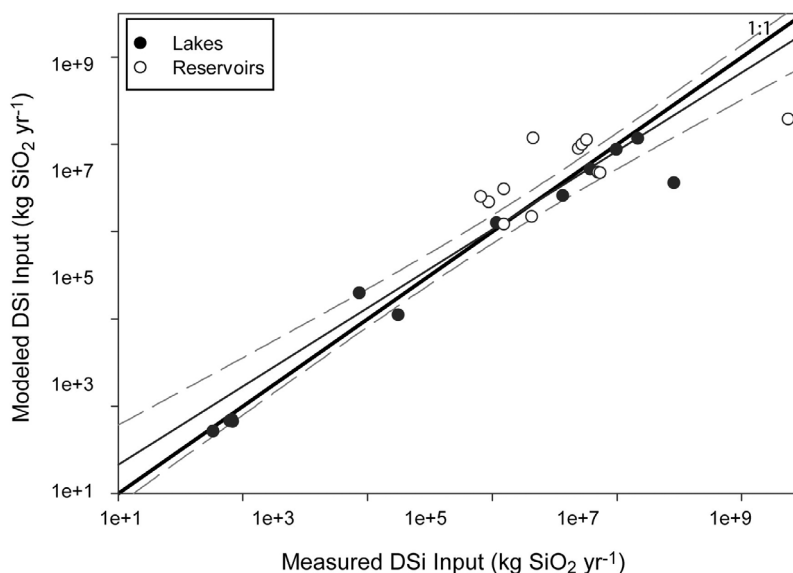

Figure 3. Comparison between measured DSi input to lakes (filled circles) and reservoirs (open circles) as reported in literature and NEWS-DSi-modeled DSi input to lakes and reservoirs (units for both axes: kg SiO$_2$ yr^{-1}). The 1:1 line (bold) and OLS regression line (black) overlap, and 95% confidence intervals (dashed lines) are shown.

This important role of small lakes acting as a biogeochemical sinks in the landscape has also been observed in similar analyses assessing the fate of carbon [*Downing et al.*, 2008] and nitrogen [*Harrison et al.*, 2009] in freshwater aquatic ecosystems. On a per unit area basis, small lakes also process 257% more DSi than large lakes (Table 3). In interpreting these model results, it is important to remember that the SiRReLa model assumes that all DSi entering surface waters in each grid cell passes through a small lake, which is most likely not the case. It should also be noted that the SiRReLa model does not account for transformation of DSi to BSi, with subsequent potential for downstream loss from lakes and reservoirs. Thus it is possible that SiRReLa somewhat overestimates the role of small lakes in removing DSi from the watershed flowpaths. Nonetheless, these results underscore the potential importance of small lakes as sinks for DSi in watersheds.

[29] Humans are increasing the number of "lakes" on the landscape via the creation of reservoirs [*Lehner et al.*, 2011]. Therefore understanding the role of reservoirs in the processing of DSi at the landscape level is of critical importance. Despite the fact that the global abundance of lakes is almost two orders of magnitude greater than that of reservoirs (3.04×10^8 lakes versus 3.77×10^6 reservoirs greater than 0.001 km^2) [*Downing et al.*, 2006], SiRReLa estimated that reservoirs remove roughly 35% of the DSi removed by lentic systems (31.0 Tg SiO$_2$ yr^{-1}). In addition, despite their comparatively low global surface area and numbers, large reservoirs appear to remove more than half as much DSi from flowpaths globally as large lakes (6.1 Tg SiO$_2$ yr^{-1} and 11.2 Tg SiO$_2$ yr^{-1} for large reservoirs and large lakes, respectively; Table 3).

[30] The relative parity of large lakes and large reservoirs with respect to DSi removal most likely results from the fact that reservoirs have very large contributing watersheds, and thus relatively large DSi loading rates (kg SiO$_2$ yr^{-1}) compared to large lakes, which generally (though not always) receive their water and Dsi from a smaller area and therefore receive less DSi input. In the large lake and reservoir data set utilized for this study the mean drainage ratio (ratio of basin surface area to lake or reservoir surface area) for reservoirs was 83, while it was just 25 for lakes [*Lehner and Döll*, 2004]. The higher drainage ratio of reservoirs resulted in higher average DSi loading to reservoirs than to lakes. In addition, because reservoirs frequently occur in human-impacted basins, they may also have higher nutrient loads than lakes, leading to more rapid DSi uptake and subsequent burial. For example, in our calibration data set, 75% of the reservoirs were reported as eutrophic whereas 80% of the lakes were not.

3.4. Regional Patterns of Lake and Reservoir Si Retention

[31] There is considerable regional variability in the potential for lakes and reservoirs to act as sinks for DSi within watersheds (Figure 4a). This spatial heterogeneity has heretofore gone largely un-quantified, in part, because there has not been a sufficiently high-resolution model to evaluate it. SiRReLa output indicates that there are a number of regions globally where lakes and reservoirs have the capacity to filter virtually all of the DSi loaded to surface waters, while in other regions lakes have very little or no capacity to remove DSi input. In general, areas where percent DSi removal approached or equaled 100% were areas with a large amount of lake surface area, low runoff rates, or both (Figure 4a). Regions where lakes and reservoirs have the capacity to remove a large proportion of the DSi added to the landscape correspond to areas with high lake densities, including boreal regions in Canada, Russia, portions of the western U.S., Eastern Brazil, Sub-Saharan Africa, northern China, Eastern Europe, Mongolia, South Africa, Australia, and parts of Argentina. The predicted DSi removal efficiency of lentic systems in many parts of the world seems quite high, but is not unreasonable given that lentic sediments average 10% BSi, with sediment BSi content ranging up to 70% in some systems (P. Frings et al., unpublished data, 2012.). In addition, to the extent we were able to validate model-predicted regional patterns they are consistent with observations of watershed DSi export and of lake sediment BSi accumulation. For example, in two otherwise broadly comparable regions, Canada and Northern Sweden, studies of ~100 lakes in both regions indicate that DSi retention in lakes is quite different, with BSi accumulation much greater in Sweden (average sediment 20% BSi by weight) [*Rosén et al.*, 2010] than in Canada (average sediment 2% BSi by weight) [*Fortin and Gajewski*, 2009].

[32] Regions with high estimated per-area rates of lake and reservoir DSi removal (kg SiO$_2$ km^{-2} yr^{-1}; Figure 4b) are somewhat different than regions where DSi removal is estimated to approach 100% of the DSi entering surface waters (Figure 4a). This pattern occurs because lake and reservoir locations do not always correspond to regions of highest DSi input. For example, while a large fraction of DSi input to lakes and reservoirs is removed in northern Canada, the rate of DSi removal is low because of low DSi inputs in this region. Basins with high rates of lentic DSi removal (kg SiO$_2$ km^{-2} yr^{-1}) occurred in both arid and humid regions, and included parts of Japan, New Zealand, the St. Lawrence River basin, the northwest U.S. and southwest Canada, southern Mexico, northern Argentina, southern Chile, northern Scandinavia, East Africa, northern India, and eastern China.

3.5. Sensitivity Analysis

[33] A number of insights emerge from a sensitivity analysis, for which a summary of results is presented in Table 4. One insight resulting from this analysis is that while SiRReLa is relatively sensitive to changes in DSi loading rates, it appears to be comparatively insensitive to alterations in hydrology. Doubling global inputs of water to the landscape (and consequently cutting water residence time in individual systems in half) only decreased predicted lentic DSi removal (Tg SiO$_2$ y^{-1}) by 21%. Decreasing water runoff by 50% resulted in a 26% increase in DSi removal. In contrast, as would be expected based on equation (4) above, doubling global inputs of DSi resulted in a doubling of DSi removal, whereas cutting DSi inputs in half resulted in a halving of lake and reservoir DSi removal. Importantly, however, interactions between runoff and DSi loading were not explored in this sensitivity analysis, and could be critical as one would expect DSi loading to increase with increasing runoff. Such a relationship has been demonstrated for several watersheds in Europe [*Humborg et al.*, 2008].
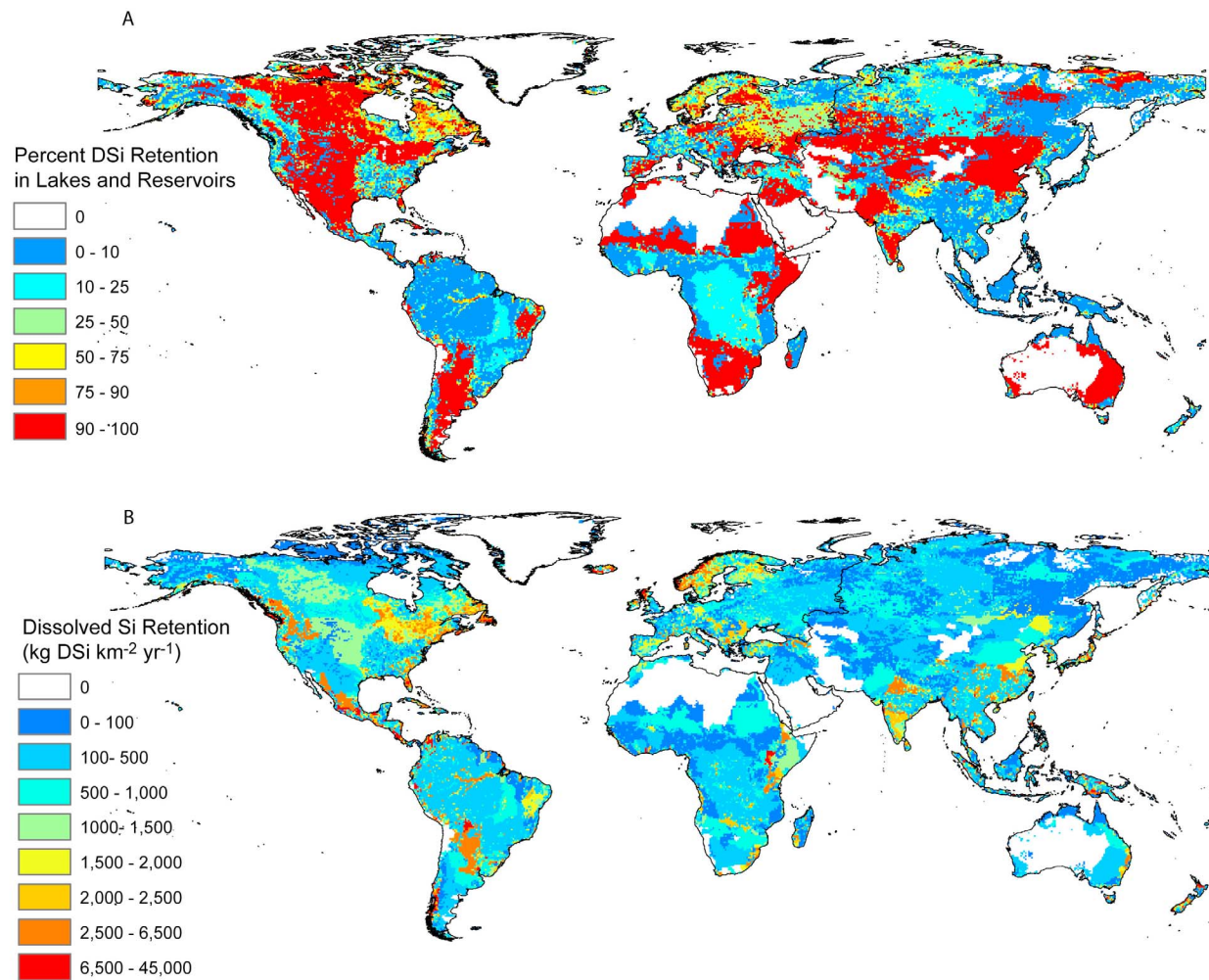
Figure 4. (a) SiRReLa-modeled global distribution of percent DSi removal by lakes and reservoirs and (b) global distribution of DSi retention rate on a per land-area basis (kg SiO_2 km^{-2} yr^{-1}).

[34] The observed difference in model response to changes in hydrologic and DSi loading is a function of the relationships between model inputs and model response variables. The relationship between percent DSi removal and water residence time is log linear (equation (5)), whereas the relationship between DSi load and DSi removal is linear. This suggests that the location of DSi inputs relative to the location of lakes and reservoirs is an important determinant of the effectiveness of lakes and reservoirs in removing DSi from surface waters (i.e., DSi inputs upstream of lakes and

Table 4. Results From a Model Sensitivity Analysis[a]

Parameter	Δ Input	Δ Prediction (%)	Range of Predicted Lake and Reservoir DSi Retention (Tg SiO_2 yr^{-1})
Runoff	Half-Double	−21% to +26%	71–112
DSi Inputs	Half-Double	−50% to +100%	44–175
Assignment of system trophic status	All Eutrophic or All Non-eutrophic	−26% to +27%	66–113
V_f	25th percentile-75th percentile (1.3–4.7 and 6.7–12.5 m yr^{-1})	−14% to +13%	77–101
c for lakes	±1 SE.	−0.03% to +0.03%	89–89*
c for reservoirs	±1 SE.	0%	89*
Minimum Lake Area	Raised to 0.01 km^2	−6%	84*
Minimum Reservoir Area	Raised to 0.01 km^2	−0.4%	89*
Minimum Lake and Reservoir Area	Raised to 0.01 km^2	−6%	84*
Small Lake and Reservoir Cutoff	Used only documented lakes and reservoirs (>0.1 km^2)	−42%	52

[a]Asterisk signifies sensitivity analysis was only run on small lakes and reservoirs.

reservoirs will be subject to retention within lentic systems, whereas DSi inputs downstream of those systems will not). This is an uncertainty in the model worthy of future investigation, and improved spatial resolution DSi loading models would constitute an important improvement over current basin-average DSi loading models, which would help address this question. Taken together, these insights suggest that, in general, DSi removal within lentic systems will be more sensitive to land use change than climate change at the global scale, though this is certain to vary by region. Climate could also significantly alter DSi transfer to surface waters by altering the balance of runoff and evapotranspiration as well as temperature-dependent and pCO_2-dependent Si weathering rates, but it is difficult to predict the magnitude, or even the direction, of these effects given the complex, interacting controls on DSi mobilization, transport, and uptake, and burial [e.g., *Cornelis et al.*, 2011].

[35] In addition, in order to assess the SiRReLa model's sensitivity to uncertainty in V_f we ran the model using low V_f (25th percentile), and high V_f (75th percentile) values. This range of variation in V_f resulted in a variation in model output that ranged between 77 and 101 Tg SiO_2 y^{-1} retained globally. Hence a 3.6-fold increase in V_f for non-eutrophied systems coupled with an 87% increase in V_f for eutrophic systems resulted in just a 27% increase in global DSi removal in lakes and reservoirs. Similarly model runs assuming that all or no lakes and reservoirs are eutrophic resulted in global total DSi retention ranging between 66 and 113 Tg SiO_2 y^{-1}. Hence, the SiRReLa model is less sensitive to variation in V_f and characterization as eutrophic or non-eutrophic than to changes in (or errors in estimates of) DSi loading.

[36] We also examined how changes in the parameterization of the Pareto distribution of lakes and reservoirs affected DSi removal by varying the parameter "c" in *Downing et al.* [2006, equations 4, 5 and 10] plus or minus one standard error. The change in model predictions resulting from this perturbation was minimal (Table 4). Finally, we examined the influence of the smallest lakes and reservoirs by excluding them from our analysis. Removing lakes smaller than 0.01 km^2 from the analysis decreased the DSi removal in lentic systems by 6%; removing reservoirs smaller than 0.01 km^2 reduced SiRReLa's estimate of small-lake Si removal by just 0.4%, possibly because DSi that would have been trapped by the smallest reservoirs is simply trapped in slightly larger reservoirs and lakes.

3.6. Conclusions, Uncertainties, and Future Directions

[37] Here we have presented a first spatially explicit, global analysis of lake and reservoir DSi removal. The SiRReLa model is a promising tool that provides insight into global rates and spatial organization of DSi removal within lentic systems. It provides initial estimates of the relative importance of natural versus man-made lakes (reservoirs) and indicates factors to which DSi removal within lakes and reservoirs is likely to be sensitive. For example, SiRReLa suggests sequestration in lentic systems is an important component of the global biogeochemical Si cycle, equivalent to an additional 19–38% of Si released from terrestrial systems and indicates regions where lentic DSi retention is likely to be especially important, and hence where DSi may be in especially short supply (hot spots in Figure 4).

[38] Recent evidence suggests that DSi inputs from terrestrial to aquatic ecosystems have changed through time due to disruption of the terrestrial Si cycle via human activities such as deforestation and agriculture [*Conley et al.*, 2008; *Struyf et al.*, 2010]. In addition, temperature and CO_2 are hypothesized to have changed weathering fluxes on century time scales [*Beaulieu et al.*, 2012]. Uncertainties in DSi inputs and changes in the factors controlling SiO_2 export from watersheds will also affect estimates of lake and reservoir retention.

[39] Clearly a number of questions remain unanswered. For example the SiRReLa model does not account for transformation of DSi to BSi, with subsequent potential for downstream loss from lakes and reservoirs. Nor does it account for any BSi input to lentic systems. Although, more attention should certainly be given to DSi-BSi interactions in future studies because the relative abundance of DSi and BSi can vary widely in lentic systems, a model characterizing DSi trapping is a reasonable place to start because BSi does not necessarily represent a large flux through river systems. For example, a global survey of rivers found that BSi is consistently the less abundant of the two forms (making up 11–34% of total bioavailable Si in large rivers) [*Conley*, 1997]. Nonetheless, a need for improved understanding of within-lake Si processing clearly remains.

[40] The apparent relative importance of small (<0.1 km^2) reservoirs in controlling DSi removal along flow paths within watersheds suggests that an important area for future research is an improved understanding of the spatial distribution and biogeochemical role of such systems. Similarly, SiRReLa assumes a very simple hydrologic linkage of small lakes with large lakes on the landscape. This could certainly be improved in future models as appropriate data becomes available to support such enhancements. Other issues that merit further investigation and may result in significant model improvements include an examination of the role of lake and reservoir hydrology and mixing regimes on DSi retention, an improved representation of inflow seasonality, improved representation of interactions with other bioactive elements such as N and P (which could grant insight into controls on transformations between DSi and BSi pools), and an improved representation of DSi cycling, including the transport, burial, remineralization, and resuspension of additional Si forms such as particulate amorphous silica. Mechanistic studies of individual lakes and reservoirs would also provide important additional insight into controls on lentic DSi dynamics and retention, with additional studies of tropical systems being an especially pressing need.

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