Exploring long term changes in silicon biogeochemistry along the river continuum of the Rhine and Yangtze (Changjiang)

Xiaochen Liu\textsuperscript{a*}, Wim Joost van Hoek\textsuperscript{a}, Lauriane Vilmin\textsuperscript{b}, Arthur Beusen\textsuperscript{a,c}, José M. Mogollón\textsuperscript{d}, Jack J. Middelburg\textsuperscript{a}, Alexander F. Bouwman\textsuperscript{a,c,e}

\textsuperscript{a} Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Princetonlaan 8A, 3584 CB Utrecht, The Netherlands

\textsuperscript{b} Deltares, P.O. Box 177, 2600 MH Delft, The Netherlands, The Netherlands

\textsuperscript{c} PBL Netherlands Environmental Assessment Agency, P.O. Box 30314, 2500 GH The Hague, The Netherlands

\textsuperscript{d} Institute of Environmental Sciences (CML), Leiden University, P.O. Box 9518, 2300 RA Leiden, The Netherlands

\textsuperscript{e} Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, PR China.

*Corresponding author: Email: x.liu@uu.nl

Contents:

Number of pages: 14
Number of tables: 4
Number of figures: 3
Number of movies: 2
Contents

SI 1. Construction of weathering

The original model proposed by Hartmann et al. \(^1\) used the following formula:

\[
F_{\text{inp,CW,DSi,c}} = \sum_{l=1}^{M} CW_{l,c} \cdot S_{l,c} \cdot T_{l,c} \cdot A_{l,c}
\]  

(S1)

This model was validated on 382 basins in the Japanese archipelago\(^2,3\). The validation showed that this model without land use and in-stream processes showed a poor agreement with observed DSi delivery in basins with relatively high fractions of natural landcover. For bigger basins, the difference between the simulated and observed DSi is bigger (see Figure S2). The integration of this factor in the Hartmann formula was not needed for the Japanese archipelago because most basins only had pristine land use. Therefore, we propose to add an additional factor “land use” to this formula. The land use factor was already described by Struyf et al. \(^4\), the formula is made by nonlinear regression based on the original 52 sub-basins.

In this study, the new formula of chemical weathering rate (ton DSi yr\(^{-1}\)) for each grid cell \(c\) is calculated as follows:

\[
F_{\text{inp,CW,DSi,c}} = L_r \sum_{l=1}^{M} CW_{l,c} \cdot S_{l,c} \cdot T_{l,c} \cdot A_{l,c}
\]  

(S2)

Where \(CW_{l,c}\) is the chemical weathering rate for lithology type \(l\) (ton DSi km\(^{-2}\) yr\(^{-1}\)), \(S_{l,c}\) is the soil shielding reduction term for specific soil types causing a reduction in the chemical weathering of the underlying lithological class \(l\), estimated on the basis of field data (no dimension; \(S_{l,c} = 0.1\) for Ferralsols, Gleysols, Acrisols, Lixisols, Nitosols and Histosols (organic soils); for all other soils \(S_{l,c} = 1\); \(A_{l,c}\) is the land area covered by each lithology class (km\(^2\)), \(M\) is the number of lithology classes. \(L_r\) is the factor that describes the impact of land use on the mobilization of Si in landscapes for each river basin \(r\).

The chemical weathering rate is obtained from:

\[
CW_{l,c} = b_{l,c} \cdot q_{\text{tot,c}}
\]  

(S3)

Where \(b_l\) is a factor for each lithological class \(l\) (ton DSi km\(^{-2}\) mm\(^{-1}\) yr\(^{-1}\)), and \(q_{\text{tot,c}}\) is the total runoff (mm yr\(^{-1}\)) in cell \(c\). The effect of temperature \((F_{T,l}, \text{no dimension})\) is obtained from the Arrhenius equation:

\[
T_{l,c} = \exp \left(\left(-\frac{E_{a,l}}{R^*}\right)\left(\frac{1}{T_{A,c}} - \frac{1}{T_0}\right)\right)
\]  

(S4)

Where \(E_{a,l}\) is the activation energy of lithology class \(l\) (J mol\(^{-1}\)) (Table S1); \(R^*\) is the gas constant (8.3144 J mol\(^{-1}\) K\(^{-1}\)), \(T_A\) is the mean air annual temperature (K) for the grid cell, and \(T_0\) (284.15 K) is the reference temperature. By introducing the impact of land use, the agreement of the model with observations improved. The land use impact on the DSi delivery based on 52 basins from Struyf et al. \(^4\) is calculated as follows:

\[
L_r = 1 - ((105.35 - 11.57 \cdot \exp(2.21 \cdot AF_{p})) / 105.35)
\]  

(S5)
Where $AF_r$ is the natural area fraction for the whole river basin $r$. 
SI 2. Validation and sensitivity analysis method

The modeled DSi concentration and discharge are validated with measurements at station Lobith in the Rhine and Datong in the Yangtze river. To express the model performance we use a statistical indicator RMSE (Root Mean Squared Error)\(^5\), It is used for comparing observations and modeled results.

\[
RMSE = \frac{100}{\bar{o}} \sqrt{\frac{\sum (o_i - M_i)^2}{n}}
\]  

(S6)

Where \(M_i\) is the simulated result \(i\), \(o_i\) is observed value \(i\), \(\bar{o}\) is mean of the observations and \(n\) is the number of observations. We consider RMSE values smaller than 50\% acceptable\(^6\).

We analysed the sensitivity of 53 parameters on the instream fluxes and exports (Table SI 3, 4) to the coastal areas. As sample method, we used Latin Hypercube Sampling (LHS)\(^7\). We used for all parameters an uniform distribution around the default values with a range of 5\%. We executed 750 runs to analyze the standardized regression coefficient (SRC) for the burial and the BSi and DSi export to the coastal seas for the period 1996-2000 for the Rhine and Yangtze. The input parameters are all described in the supplementary information section SI 3. We only highlight those input parameters which have a SRC value within the range SRC>0.2 and SRC <-0.2 in Table SI 3.

The uncertainty contribution of each parameter \((X_i)\) to model outcome \(Y\) is assessed with linear regression\(^6,8\):

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_n X_n + e
\]  

(S7)

where \(\beta_i\) is the coefficient for regression of parameter and \(e\) is the error of the approximation of \(Y\). The linear regression model can be assessed for parameter contribution analysis by the coefficient of determination \(R^2\), which means the \(Y\) variation can be explained by \(Y\)-\(e\).

The Standardized Regression Coefficient \((SRC_i)\) is calculated to scale \(\beta_i\) to the relative contribution of variation of \(Y\), the standard deviations of \(X_i\) and \(Y\) as follows:

\[
SRC_i = \frac{\beta_i \sigma_{X_i}}{\sigma_Y}
\]  

(S8)

\(SRC_i\) is independent of units and scale of parameters. The \(SRC_i\) take value between -1 and 1 and is independent of units scale and size. The positive \(SRC_i\) value indicates that an increasing parameter value leads to output \(Y\) increase. The negative \(SRC_i\) indicates a decreasing output \(Y\) with an parameter value increase.
### SI 3. The parameters and values used in DISC-SILICON

Table SI 1. List of parameters and their values as used in DISC-SILICON

| Parameters                      | Description                                      | Default values | Unit   | Sources                      |
|---------------------------------|--------------------------------------------------|----------------|--------|------------------------------|
| $k_{\text{max.growth.pelagic}}$ | Max growth rate for pelagic diatoms               | 0.085          | h⁻¹    | Sferratore.⁹                 |
| $k_{\text{max.growth.benthic}}$ | Max growth rate for benthic diatoms               | 0.04           | -      | Sferratore⁹                  |
| $T_{\text{opt.growth}}$        | Optimal water temperature for primary production | 18             | °C     | Sferratore⁹                  |
| $T_{\text{sigma.growth}}$      | Standard deviation of temperature for primary production | 13             | °C     | Garnier, et al.ⁱ⁰            |
| $K_{\text{DSi,PP}}$            | DSi half saturation concentration                 | 7              | µmol Si/L | Sferratore⁹                  |
| $k_{\text{lysis}}$             | Lysis rate of diatoms                             | 0.004          | h⁻¹    | Garnier, Billen and Palfner¹⁰|
| $V_{f}$                        | Lysis amplification factor at high temperature/algal biomass | 20             | -      | Garnier, Billen and Palfner¹⁰|
| $PHYP_{\text{-Si}}_{\text{lim, pelagic/benthic}}$ | Threshold diatom concentration for mortality (mortality occurs if concentration > $PHYP_{\text{-Si}}_{\text{lim}}$) | 26.83          | µmol Si/L | Garnier, Billen and Palfner¹⁰*|
| $k_{\text{Burial max}}$        | Maximum burial rate for deposited diatom biomass  | 0.0005         | h⁻¹    | Billen, et al.¹¹             |
| $SED_{\text{lim}}$             | Threshold sediment stock;                         | 500.00         | g /m²  | Billen, Garnier and Silvestre¹¹|
| $k_{\text{morta}}$             | Mortality rate of diatoms                         | 0.004          | h⁻¹    | Garnier, Billen and Palfner¹⁰|
| $k_{\text{resp}}$              | Respiration rate of diatoms                       | 0.003          | h⁻¹    | Garnier, Billen and Palfner¹⁰|
| $k_{\text{excr}}$              | Excretion rate of diatoms                         | 0.002          | h⁻¹    | Garnier, Billen and Palfner¹⁰|
| $V_{\text{sed,PIM}}$           | Settling velocity of PIM                          | 0.05           | h⁻¹    | Garnier, Billen and Palfner¹⁰|
| $k_{\text{ero}}$               | Erosion coefficient                               | 20000          | ton/km²| Vilmin, et al.¹²             |
| $k_{\text{sed}}$               | Half-saturation constant                          | 1*10⁻⁶         | km     | Vilmin, Flipo, De Fouquet and Poulin¹²|
| $V_{\text{sed,Det_Si_Pelagic}}$| Settling velocity of Det_Si_Pelagic               | 0.05           | h⁻¹    | Garnier, Billen and Palfner¹⁰|
| Parameter                           | Description                                                                 | Value  | Unit       | Reference                      |
|------------------------------------|------------------------------------------------------------------------------|--------|------------|--------------------------------|
| $k_{\text{max}_\text{Det_Si_Pelagic dissolution}}$ | Maximum dissolution rate of pelagic Det_Si                                   | 0.002  | h$^{-1}$   | Garnier, Billen and Palfner $^{10}$ |
| $T_{\text{opt Det_Si_Pelagic dissolution}}$   | Optimal temperature for dissolution of pelagic Det_Si                       | 25     | °C         | Garnier, Billen and Palfner $^{10}$ |
| $T_{\sigma_\text{Det_Si_Pelagic dissolution}}$ | Standard deviation of temperature for dissolution of pelagic Det_Si        | 15     | °C         | Garnier, Billen and Palfner $^{10}$ |
| $k_{\text{max}_\text{Det_Si_Benthic dissolution}}$ | Maximum dissolution rate of benthic Det_Si                                  | 0.002  | h$^{-1}$   | Garnier, Billen and Palfner $^{10}$ |
| $\eta_{\text{water}}$               | The effect of water on light extinction in the water column                | 0.8    | m$^{-1}$mg$^{-1}$L | Scheffer $^{13}$ |
| $\eta_{\text{Det_Si_Pelagic}}$       | The effect of Det_Si_Pelagic on light extinction in the water column       | 0.05   | m$^{-1}$mg$^{-1}$L | Scheffer $^{13}$ |
| $\eta_{\text{PHYP_Si_Pelagic}}$      | The effect of PHYP_Si on light extinction in the water column              | 0.05   | m$^{-1}$mg$^{-1}$L | Scheffer $^{13}$ |
| $\eta_{\text{PIM}}$                  | The effect of PIM on light extinction in the water column                  | 0.03   | m$^{-1}$mg$^{-1}$L | Scheffer $^{13}$ |
| $k_{I,\text{PHYP_Si_Benthic}}$       | Half saturation of light limitation with Michaelis-Menten for PHYP_Si Benthic | 12.5   | W m$^{-2}$ | Garnier, Billen and Palfner $^{10}$ |
| $k_{I,\text{PHYP_Si_Pelagic}}$       | Half saturation of light limitation with Michaelis-Menten for PHYP_Si Pelagic| 25     | W m$^{-2}$ | Garnier, Billen and Palfner $^{10}$ |

* C: Chlorophyl ratio of 0.035 mg C. µgChl yr$^{-1}$ and the Redfield molar ratio C:Si 106:15.
SI 4. Sensitivity analysis results

The sensitivity analysis results in Table SI 2 for Rhine and Table SI 3 for Yangtze. The following model output was analyzed: total Si export (sum of DSi and BSi) to mouth (TSi_export), dissolved Si export to mouth (DSi_export), Phytoplankton Si and Detritus Si export to mouth (BSi_export), Phytoplankton Si and Detritus Si burial (BSi_burial), pelagic phytoplankton primary production (PP_pelagic), benthic phytoplankton primary production (PP_benthic).

Table SI 2. Standardized regression coefficient (SRC) representing the relative sensitivity of the model performance for the Rhine river to the variations of 53 model parameters. Parameters which have no significant SRC values for none of the outputs are not shown. The description, default value and unit of the input parameters is provided in Table SI 1.

| Parameters                        | TSi export | DSi export | BSi export | BSi burial | PP_pelagic | PP_benthic |
|-----------------------------------|------------|------------|------------|------------|------------|------------|
| Solar radiation                  | -0.06      | -0.10      | 0.14       | 0.20       | 0.18       | 0.32       |
| Temperature                      | 0.01       | 0.03       | -0.08      | -0.03      | 0.55       | 0.11       |
| Slope                            | 0.08       | 0.02       | 0.23       | -0.25      | -0.01      | -0.03      |
| Discharge                        | 0.19       | 0.02       | 0.66       | -0.60      | -0.05      | -0.06      |
| $K_{I, PHYP \_ Si, Pelagic}$      | 0.01       | 0.02       | -0.03      | 0.04       | -0.02      | -0.08      |
| $T_{opt \_ Det \_ Si, Benthic \_ dissolution}$ | -0.06      | -0.12      | 0.22       | 0.20       |            |            |
| $V_{sed, Det \_ Si, Pelagic}$    | -0.09      | -0.34      | 0.29       |            |            |            |
| $T_{opt \_ growth}$              | 0.05       | 0.08       | -0.10      | -0.17      | -0.50      |            |
| $T_{sigma \_ Det \_ Si, Pelagic \_ dissolution}$ | -0.03      | -0.04      | 0.05       | 0.09       | 0.23       |            |
| $k_{max \_ growth \_ pelagic}$   | -0.04      | -0.06      | 0.09       | 0.13       | 0.32       |            |
| $PHYP \_ Si_{lim, pelagic}$      | -0.03      | -0.05      | 0.10       | 0.09       | 0.28       | 0.03       |
| $K_{I, PHYP \_ Si, Benthic}$     | 0.04       | 0.07       | -0.09      | -0.14      | -0.34      |            |
| $k_{max \_ growth \_ benthic}$   | -0.08      | -0.12      | 0.17       | 0.25       | 0.63       |            |
| $K_{morta}$                      | 0.04       | 0.07       | -0.09      | -0.13      | -0.35      |            |
| PIM load2river                   | -0.07      | -0.02      | -0.22      | 0.23       |            |            |
| DSi weathering input             | 0.96       | 0.97       | 0.03       | 0.06       | 0.02       | 0.05       |

Values without color indicate -0.2<SRC<0.2; values with green and pink colors indicate values < -0.2 and > 0.2 respectively. Positive values indicate that a higher input parameter value generates a higher model output variable, and negative values indicate that a higher input parameter value generates a lower model output variable.
Table SI3. Standardized regression coefficient (SRC) representing the relative sensitivity of the model performance for the Yangtze river to the variations of 53 model parameters. Parameters which have no significant values for none of the outputs are not shown. The description, unit and default value of the input parameters is provided in Table SI 1.

| Parameters                                | TSi_Export | DSI_Export | BSi_Export | BSi_Burial | PP_PHYP_ambient_Pelagic | PP_PHYP_ambient_Benthic |
|-------------------------------------------|------------|------------|------------|------------|-------------------------|-------------------------|
| Solar radiation                           | -0.09      | -0.14      | 0.27       | 0.30       | 0.22                    | 0.29                    |
| Temperature                               | 0.14       | 0.17       | -0.19      | -0.34      | 0.19                    | 0.13                    |
| Discharge                                 | 0.09       | 0.50       | -0.33      | -0.07      | -0.06                   |                         |
| $T_{\text{opt Det Si Benthic dissolution}}$ | -0.15      | -0.20      | 0.31       | 0.39       | -0.02                   | -0.03                   |
| $V_{\text{sed Det Si Pelagic}}$           | -0.12      | -0.08      | -0.26      | 0.27       | -0.01                   |                         |
| $k_{\text{max growth pelagic}}$           | -0.14      | -0.20      | 0.35       | 0.32       | 0.47                    | -0.08                   |
| $k_{\text{PHYP Si lim pelagic}}$          | -0.09      | -0.15      | 0.33       | 0.23       | 0.45                    | -0.05                   |
| $k_{\text{PHYP Si lim Benthic}}$          | 0.05       | 0.06       | -0.07      | -0.13      | 0.02                    | -0.31                   |
| $k_{\text{max growth benthic}}$           | -0.14      | -0.16      | 0.15       | 0.27       | -0.03                   | 0.65                    |
| $k_{\text{morta}}$                        | 0.03       | -0.02      | -0.08      | 0.02       |                         | -0.24                   |
| $PHYP_\text{Si lim benthic}$              | -0.05      | 0.10       | 0.11       | -0.01      | 0.33                    |                         |
| DSI weathering input                      | 0.78       | 0.76       | 0.06       | 0.16       | 0.08                    | 0.10                    |

* Values without color indicate -0.2<SRC<0.2; values with green and pink colors indicate values <-0.2 and > 0.2 respectively. Positive values indicate that a higher input parameter value generates a higher model output variable, and negative values indicate that a higher input parameter value generates a lower model output variable.

For both rivers, Rhine and Yangtze, the TSi_Export and DSI_Export are strongly controlled by DSI_Input from weathering. This also shows that DSI is the main source of the total Si_Export. The SRC in the Yangtze (0.78) and Rhine (0.96) are both much higher than values for other model parameters.

The BSi_Export in the Yangtze is negatively influenced by the detritus sedimentation velocity of waterbodies. In contrast, there is a positive effect of solar radiation, discharge, optimal temperature for dissolution of Det_Si_Pelagic, max growth rate for pelagic diatoms and the diatoms threshold over which mortality is triggered. Compared with the Yangtze, the BSi_Export in the Rhine is sensitive to the width of waterbodies, slope and particulate inorganic matter. This difference is because the Rhine has no major reservoirs, causing the average water travel time to be much shorter than that in the Yangtze.

The BSi_Burial in both river basins are negatively influenced by temperature (higher temperature causing higher dissolution of Det_Si and therefore lowering BSi Burial) and discharge (higher discharge causing higher flow velocity, more resuspension, less BSI_Burial), and positively controlled by solar radiation, settling velocity of Det_Si_Pelagic, max growth rate for benthic/pelagic diatoms.

For both pelagic and benthic primary production, the results of the sensitivity analysis show that solar radiation, the length of waterbodies, half saturation of light limitation, max...
growth rate, threshold over which mortality is triggered and the mortality rate are important parameters.

Table SI 4. Basin Reservoir volume, Natural area fraction, Dominant Lithology for the Rhine and Yangtze rivers.

| Property                   | Rhine                          | Yangtze                         | References* |
|----------------------------|--------------------------------|---------------------------------|-------------|
| Reservoir volume (km³)     | 0.6 in 1950 1.5 in 2000        | 0 in 1950 103.3 in 2000         | This study  |
| Natural area fraction      | 42% in 1950 47% in 2000        | 73% in 1950 33% in 2000         | This study  |
| Dominant Lithology         | Mixed consolidated sedimentary and Alluvial deposits | Silici-clastic Sedimentary Rocks and Carbonated consolidated sedimentary | 14          |
Figure S1. Scheme of the IMAGE-DGNM framework
Figure S2. Modeled according to Hartmann et al (2014) vs Modeled minus Observed values for all the 382 basins. Red arrow indicates that the differences between simulations and observations are increasing.
Figure S3. Comparison of fluxes to and from the DSi pool in the Rhine (a) and Yangtze (b) in the period 1900-2000. PP = Primary production = F5/F13, RE = Respiration = F6/F12, EX = Excretion = F6/F12, DI = Dissolution = F4/F14, Input = Input to streams, Export = Export to mouth.
References

1. Hartmann, J.; Moosdorf, N.; Lauerwald, R.; Hinderer, M.; West, A. J., Global chemical weathering and associated p-release - the role of lithology, temperature and soil properties. *Chemical Geology* **2014**, *363*, 145-163.
2. Hartmann, J., Bicarbonate-fluxes and CO$_2$ consumption by chemical weathering on the Japanese Archipelago - Application of a multi-lithological model framework. *Chemical Geology* **2009**, *265*, (3-4), 237-271.
3. Kobayashi, J., A chemical study on the average quality and characteristics of river waters of Japan. *Nogaku Kenkyu* **1961**, *48*, (2), 63-106.
4. Struyf, E.; Smis, A.; Van Damme, S.; Garnier, J.; Govers, G.; Van Wesemael, B.; Conley, D. J.; Batelaan, O.; Frot, E.; Clymans, W.; Vandevenne, F.; Lancelot, C.; Goos, P.; Meire, P., Historical land use change has lowered terrestrial silica mobilization. *Nat. Commun.* **2010**, *1*, (1), 129.
5. Chai, T.; Draxler, R. R., Root mean square error (RMSE) or mean absolute error (MAE)?– Arguments against avoiding RMSE in the literature. *Geoscientific Model Dev.* **2014**, *7*, (3), 1247-1250.
6. Beusen, A. H. W.; Van Beek, L. P. H.; Bouwman, A. F.; Mogollón, J. M.; Middelburg, J. J., Coupling global models for hydrology and nutrient loading to simulate nitrogen and phosphorus retention in surface water &ndash; description of IMAGE–GNM and analysis of performance. *Geoscientific Model Dev.* **2015**, *8*, (12), 4045-4067.
7. Saltelli, A.; Chan, K.; Scott, E. M., *Sensitivity analysis*. Wiley and Sons: Chichester, UK, 2000.
8. House, W. A.; Leach, D. V.; Armitage, P. D., Study of dissolved silicon, and nitrate dynamics in a fresh water stream. *Water Research* **2001**, *35*, (11), 2749-2757.
9. Sferratore, A. Modelling the transfer, transformation and retention of silica along aquatic continuums: an upgraded deterministic approach. Thesis. Université Paris VI, 2006.
10. Garnier, J.; Billen, G.; Palfner, L., Understanding the oxygen budget and related ecological processes in the river Mosel: The RIVERSTRAHLER approach. *Hydrobiologia* **2000**, *410*, 151-166.
11. Billen, G.; Garnier, J.; Silvestre, M., A simplified algorithm for calculating benthic nutrient fluxes in river systems. *Annales de Limnologie* **2015**, *51*, (1), 37-47.
12. Vilmin, L.; Flipo, N.; De Fouquet, C.; Poulin, M., Pluri-annual sediment budget in a navigated river system: the Seine River (France). *Science of the Total Environment* **2015**, *502*, 48-59.
13. Scheffer, M., *Ecology of shallow lakes*. Springer Science & Business Media: 2004; Vol. 22.