Transport of dissolved Si from soil to river: a review

Benedicta Ronchi, Floor Vandevenne, Ana Lúcia Pena Barão, Wim Clymans, Eric Struyf, Okke Batelaan, Alain Dassargues, Gerard Govers

Benedicta Ronchi, Wim Clymans, Okke Batelaan, Alain Dassargues, Gerard Govers

Earth and Environmental Sciences, K. U. Leuven, Celestijnenlaan 200E 2410, 3001 Heverlee, Belgium

Floor Vandevenne, Ana Lúcia Pena Barão , Eric Struyf

Ecosystem Management Research Group, Department Biology, University Antwerp, Campus Drie Eiken,D.C.116, Universiteitsplein 1, 2610 Wilrijk, Belgium

Okke Batelaan

Department of Hydrology and Hydraulic Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

Alain Dassargues

Hydrogeology and Environmental Geology, Dept. of Architecture, Geology, Environment and Civil Engineering (ArGEnCo) and Aquapole, Université de Liège, B.52/3 Sart-Tilman, BE-4000 Liège, Belgium.

Abstract

This paper reviews the processes which determine the concentrations of dissolved silicon (DSi) in soil water and proposes a mechanistic model for understanding the transport of Si through a typical podzol soil to the river. DSi present in natural waters originates from the dissolution of mineral and amorphous Si sources in the soil. However, the DSi concentration in natural waters will be dependent on both dissolution and deposition/precipitation processes. The net DSi export is controlled by soil composition like (mineralogy and saturated porosity) as well as water composition (pH, concentrations of organic acids, CO_2 and electrolytes). These state variables together with production, polymerization and adsorption equations constitute a mechanistic framework determining DSi concentrations. For a typical soil profile in a temperate climate, we discuss how the values of these key controls differ in each soil horizon and how it influences the DSi transport. Additionally, the impact of external forcings such as seasonal climatic variations and land use, is evaluated. This model is a first step to better understand Si transport processes in soils and should be further validated with field measurements.

Keywords: Si transport; model; land use; biogenic Si

1. Introduction

In aquatic systems, dissolved Si (DSi) is an important nutrient. Dissolved Si is mainly delivered to the oceans by river discharge: rivers provide more than 80% of the total input of dissolved silicon (DSi) into the oceans [136], the rest being provided by aeolian dust input and ocean floor weathering. Given the relatively low residence time of DSi in the ocean reservoir (ca. 400 yrs, [136]) , the delivery of riverine to the oceans is critical for maintaining primary productivity in the world oceans and plays a crucial role in the biological uptake of CO_2 through the so-called biological carbon pump [76].

Land-river Si fluxes depend on the relative contribution of different Si sources and on the type of processes (e.g. biological, physico-chemical, pedological) occurring along the pathway [125 32]. The particulate Si fraction in soils and bedrock consists of well-crystallized minerals (e.g. quartz, other primary and secondary silicates) and amorphous Si (ASi) [119, 32]. ASi can be subdivided in biogenic silica (i.e. plant Si bodies called phytoliths) and non-crystalline inorganic Si fractions (i.e. formed by pedogenic processes). In most ecosystems the biogenic constituent is the most abundant. These ASi fractions are important for Si delivery: (i) they can be up to 17 times more soluble than quartz [54] and their dissolution may therefore constitute the most important source of DSi delivered to rivers by groundwater and/or surface and subsurface runoff [62] and (ii) ASi may be directly delivered to aquatic systems by physical erosion during erosion events [124, 22].

Thus, DSi concentrations in rivers will to a large extent be controlled by DSi concentrations in soil pore water. DSi concentrations in soil water will have an important effect on DSi concentrations in and DSi delivery to rivers: several studies have shown during large runoff events often consists for a large part of soil pore water that is pushed out of the soil system by the new precipitation Understanding the mechanisms controlling DSi dynamics within soils is therefore key to understanding spatial and temporal varitiations in river water and , hence, in Si delivery to the ocean.

A wide range of processes other than dissolution control soil pore water DSi concentrations: adsorption on Fe-and Al-oxides, polymerization, formation of nanocolloïds, precipitation of secondary minerals and uptake by vegetation [41, 137, 32,98, 2778] which complexes the comprehension of land-river Si transfer. These processes are described separately by physically based equations but models combining all processes do not yet exist. Such a model shoud not only consider soil processes but should account for the effects of vegetation as vegetation profoundly affects the intensity of the biogeochemical Si cycling [7, 2, 13, 30]. The latter implies that land use may strongly affect DSi delivery, as land use changes will not only affect vegetation but also soil hydrology and soil chemistry. . Finally, at the landcape scale, geomorphological and hydrogeological features as these control which ASi and DSi reservoirs contribute to Si delivery at what time. Indeed, the contributions of various reservoirs will not be constant through time but will vary depending on hydrological conditions (moisture status) as well as vegetation dynamics.

Si pools and fluxes in landscapes have previously been discussed in the review of Sommer et al. [125]. Street-Perrott and Barker [126] emphasized the importance of coupling the the Si and C

77 cycles, while Cornelis et al. [32] focused their review on the impact of the soil-plant system on
78 DSi in weathering-limited and weathering-unlimited environments. While these reviews provide a
79 good overview of the state of the art of our knowledge with respect to Si cycling, they do not
80 discusss how this knowledge can be integrated in a mechanistic modeling framework that might be
81 used to quantitatively predict (changes in) DSi concentrations and fluxes in soils and DSi delivery
82 from soils to rivers. Other catchment studies developed empirical equations to calculate the DSi
83 concentrations in groundwater and soil pore water based on measurements [122, 62]. These are,
84 however, site specific, non-transferable equations.
85

86 In this review, the DSi delivery at soil profile scale from a typical podzol soil to the river ise
87 analysed. In contrast to earlier work, we establish a framework of mechanistic equations that may
88 be used to model DSi transport. An overview is given of all equations describing dissolution,
89 adsorption and uptake of Si by plants. We propose these equations to predict expected variations
90 of Si concentrations within soil profiles and discuss which further steps are needed to develop a
91 fully operational model of DSi production and delivery under different land uses. Finally, we
92 discuss how the different processes are affected by land-use and seasonal variations in vegetation
93 for catchments with comparable climate, lithology but covered by grassland, cropland or forest.
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96
97

98 # 2. Sources and sinks of Si in soils

99 ## 2.1. Typology of Si-particles

100 Silica is the second most abundant element in the earth crust and is present in different forms. In
101 soils, mineral Si (MSi) is dominant but amorphous Si (BSi) is also present in significant amounts
102 [126] (Figure 1). Mineral silicates can be subdivided in different categories: the primary minerals
103 formed by magmatic crystallization (quartz, feldspars,…) and the secondary minerals developed
104 during soil formation. The secondary phases, concentrated in the clay fraction of soils, can be well
105 crystallized like phyllosilicates [73] , micro-crystalline (autigenic quartz, Opal CT, chalcedon) or
106 short-range ordered (imogolite, proto-imogolite, allophane) [45, 144, 94]. Amorphous forms of
107 mineral Si are non-crystalline inorganic particles forming opal-A or volcanic glasses. Amorphous
108 coatings of opal can also cover secondary minerals [98, 19]. Amorphous Si can be of biogenic
109 origin. In this biogenic Si pool, the phytogenic Si (including phytoliths) is the most important
110 component. Phytoliths are formed by plants who take up DSi from the soil solution , which then
111 precipitates as phytoliths in plant roots, stems and leaves/needles. When dead plant material is
112 decomposed, the phytoliths are released to the topsoil. Phytoliths are not the only important form
113 of ASi in soils: sponge spicules, diatoms and testate amoebae are also important components of

biogenic Si ([119, 125], especially in wetlands [128] and forests[4]. A classification of all types of Si-particles is presented in Fig. 1.

Although atmospheric inputs are low in comparison to other Si fluxes in the soil-plant system they deserve special attention because they are a net source of DSi for the soil-plant system. Aeolian erosion can collect Si-rich dust from soils and potentially transport it to other continental regions or the ocean. As wind forces are very variable regionally and the mineralogical composition of aeolian dust is dependent on the soil of origin, the process is difficult to quantify at larger scales. Atmospheric inputs from aeolian deposition have been estimated to range from 0.04 to 2 kg Si ha^{-1} $year^{-1}$ for temperate and tropical forests in non-volcanic areas [126]. The spread of volcanic ashes containing ASi in the form of volcanic glass is generally limited to volcanic regions only, but occasionally volcanic dust is dispersed over large areas, depending on the type and magnitude of the eruption as wells as on the meteorological conditions at the moment of eruption. ASi input by rainfall is of the same order of magnitude than that by dust deposition: the maximum value found is 3±2 kg Si ha^{-1} yr^{-1} [32].

2.2. Si dissolution and weathering

The dissolution of silicates and amorphous Si generally forms monosilicic acid (H_4SiO_4; DSi):

$$SiO_{2(s)} + 2H_2O_{(aq)} \leftrightarrows H_4SiO^0_{4(aq)} \quad (1)$$

Dissolution can also lead to the formation of polysilicic acid but its stability is relatively low. Depending on pH, temperature and composition of natural waters, depolymerisation of polysilicic acid takes place in a few hours or days[40].

In contrast to quartz, which is highly ordered, amorphous silica is a short-range order crystal composed of loosely packed silica tetrahedrals. Consequently, the solubility of amorphous silica is much higher (1.8-2mM Si under laboratory conditions) than that of quartz (0.10-0.25mM Si).

It is often assumed that the Si concentration in natural waters is mainly controlled by mineral silicate hydrolysis (Equation 1): 45% of the dissolved load in rivers is attributed to mineral (?) Si weathering. [130]. [57, 93, 106115]. The mass-balance for a specific element in an aequous solution resulting from dissolution of mineral phases can be calculated as follows for for j reactants and p product phases:.

$$\sum_{j=1}^{i} MTC_p \alpha_p^i = \Delta m_i = m_{i(final)} - m_{i(initial)} \quad (2)$$

Where MTC **is the mass-transfer coefficient for any phase (*p*) in moles, *α* the stoichiometric coefficient of element *i* in phase *p*, *m* the total moles of element *i* in the initial and final solutions [5, 16].** However, the composition of natural waters is not only dependent on mineral

composition: dissolution is also influenced by temperature, reactive surface and pH. Si solubility is relatively constant between pH 2 and 8.5 but increases drastically when pH>9 or pH < 2 (?). Bases dissolve ASi, imogolite and allophone while acidic conditions enhance the desorption of adsorbed Si [119]. Gérard et al. [62] take account of the temperature dependency of the Arrhenius equation (Equation 4) as well as pH when calculating the dissolution rate constant for silicate minerals as follows:

$$r_d = k_d S \{H^+\}^n \left(1 - e^{-A_r/RT}\right) \quad (3)$$

$$\text{with } A_r = -RTln\left(\frac{Q}{K}\right) \quad (4)$$

in which r_d is the dissolution rate (mol kg^{-1} s^{-1}), k_d is the dissolution rate constant (mol m^{-2} s^{-1}), S is the reactive surface of the mineral ($m^2kgH_2O^{-1}$), {H+} is the activity of protons in the reacting solution, n is an experimental exponent and Q is the ionic activity product of the reaction. The temperature dependence of k_d is described by

$$k_d(T) = k_d^0 e^{-E_a/RT} \quad (5)$$

in which k_d^0 is k_d at a given reference temperature, E_a is the apparent activation energy of the dissolution reaction (kJ mol^{-1}), R is the gas constant ($8.32x10^{-3}$ kJ mol^{-1} K^{-1}) and T is the temperature (K).

The equations above describe the mineral dissolution in deionized water: however, the presence of electrolytes can increase dissolution rates. Water dipoles attack more easily and efficiently mineral surfaces on which cations are adsorbed. To correct for this, the Langmuir adsorption model can be integrated [44] in eq. 4:

$$k_d^{corr} = k_d^{Na^+}\sigma_{Na^+} + k_d^{Mg^{2+}}\sigma_{Mg^{2+}} + k_d^{Ca^{2+}}\sigma_{Ca^{2+}} + k_d^0\left[1 - \left(\sigma_{Na^+} + \sigma_{Mg^{2+}} + \sigma_{Ca^{2+}}\right)\right] \quad (6)$$

$$\text{with } \sigma_A = \frac{K_{ad}^A m_A}{1 + K_{ad}^{Na^+} m_{Na^+} + K_{ad}^{Mg^{2+}} m_{Mg^{2+}} + K_{ad}^{Ca^{2+}} m_{Ca^{2+}}} \quad (7)$$

Where σ_A is the fraction of sites occupied by cation A, m_A the molal concentration of the cation and K_{ad}^A the equilibrium adsorption coefficient of the cation. The last term of eq. 6 allows to account for adsorbed protons on remaining sites as adsorption is a competitive process[66].

A further complicatioln is that water acidification by CO_2 production ($P_{CO_2}^m$) and the presence of organic acids ($[org]$) also need to be accounted for: [131, 132]:.

$$r_j = k_{H^+}\frac{\{H^+\}^n}{\{M\}^x\{Al^{3+}\}^y} + \frac{k_{H_2O}}{\{Al^{3+}\}^u} + k_{CO_2}.P_{CO_2}^m + k_{org}[org]^{0.5} \quad (8)$$

Where r_j is the dissolution rate of mineral j, k_i is the rate coefficient, *M* the base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+), *n ,x , y, u* and *m* apparent reaction orders to be determined experimentally. Similar to eq. 3, the first term of the equation accounts for the effect of pH and solution composition, but adding this time the effect of Al^{3+}. This term stands for formation and decomposition of activated surface complexes. The concentrations of base cations and Al are pH-

dependent: in acid water the base cations on the exchange complex are replaced by H_3O^+. and $Al(OH)_3$ dissolution is enhanced. After the replacement of exchange complexes by H_3O^+, an alkali-depleted layer enriched in Si and /or Al forms around the mineral. This residual layer will dissolve slowly. Al therefore has a complex role in the dissolution of minerals as its concentration is not only pH-dependent (like showed in the first term) but also interacts in the residual layer: t his interaction is accounted for in the third term of eq. 8. The last two terms calculates the rate contribution due to the described acidification factors[5].The presence of CO_2 accelerates the dissolution by providing protons . Berg and Banwart [X] suggest that at neutral to near basic pH weathering will be enhanced by the reactive carbonate complexes sorbed on mineral surfaces. Drever and Stillings [46] discussed the effect of organic acids on dissolution rates. Their presence can significantly increase dissolution rates drive dissolution rates far from equilibrium by lowering the pH but this process seems only to be significant below pH 5. Pokrovski and Schott [112] observed that aqueous Si and organic ligands did not easily form complexes. This observation implies that the adsorption of organic ligands is rather limited to quartz. Drever and Stillings [46] suggest that organic acids influence the silicate weathering indirectly as secondary iron and aluminium hydroxides dissolve first. In aluminosilicates the Al-O bounds will break more rapidly than the stronger Si-O bounds [108,109, 59,37- 39, 103]. The resulting higher permeability induces an accelerated transport thereby increasing weathering.

In the equations above water availability is assumed to be non-limiting. However dissolution and hydrolysis are are only possible by contact between water and minerals. It is therefore logical to assume that the total weathering amount (?) (R_w) within a soil profile is proportional to the soil water content (θ) as well as the time (t) of the weathering processes [5]. As the soil composition and water content vary from one horizon to another, the total weathering rate has to be calculated for each horizon and finally summed for the whole soil column.

$$R_w = \sum_{i=1}^{horizons} \theta_i \sum_{j=1}^{minerals} r_j . t \qquad (9)$$

It is generally assumed that the weathering processes of silicates are accelerated in the vadose zone, especially in the root zone where biological activity is more important [3, 134]. This is mainly due to… However, silicate weathering is also known to increase with increasing concentrations of the acids H_2CO_3 and H_2SO_4 [87, 83]. These acids are produced in the saturated zone by mineralization processes of organic compounds and sulfides oxidation respectively [83]. The effect of H_2CO_3 is the same process as observed by Berg and Banwart [X] and is is accounted for in equation 8 by the third term. However, the of H_2SO_4 on Si weathering has hitherto never been formulated in a similar equation.

The combination of existing knowledge, as presented above, allows us to propose a new set of equations to approximate the amount of Si dissolved in soil from a diverse range of sources:

$$r_{d\,total} = \sum_{j=1}^{horizons}(\theta_j \sum_{i=1}^{soil\ comp} \alpha_i r_{d_i}\ ) \quad (10)$$

$$r_{d\,hor} = \theta \sum_{i=1}^{soil\ comp} \alpha_i r_{d_i} \quad (11)$$

$$r_{d_i} = k_d^{corr}\ \ S\{H^+\}^n \left(1 - e^{-A_r/RT}\right)\left(\frac{k_{H_2O}}{\{Al^{3+}\}^u} + k_{CO_2}.P_{CO_2}^m + k_{org}[org]^{0.5} + \mathrm{k}_{\mathrm{SO_4^{2-}}}[\mathrm{SO_4^{2-}}]^{\mathrm{a}}\right) \quad (12)$$

$$\text{With } k_d^{corr} = \left(\sum \sigma_{\mathrm{A}}\, \mathrm{k_d^A}\right) + k_d^0\left[1 - \left(\sum \sigma_{\mathrm{A}}\right)\right] \quad (13)$$

Where A = Na^+, Ca^{2+}, Mg^{2+}, K^+ and Al^{3+}. Knowing the *fraction* of each soil component in the soil (α in %), a weighted rate $r_{d\,hor}$ can be calculated for each soil horizon *j*. The $r_{d\,total}$ is the rate for a whole soil profile. These deterministic equations can be used to calculate the weathering and mobilization potential of DSi to soil water as they are based on known processes affecting the Si dissolution rate. Using deterministic equations is a precise but time-consuming approach since a lot of parameters need to be known (e.g. precise soil and water compositions, precise data base of k_d^0).

. As k_d^0 is different for each source type, r_d has to be calculated for each Si soil component *i* (r_{d_i}), in other words for each mineral.

Current approaches modeling DSi dynamics generally ignore the biogenic and pedogenic Si pools as potential DSi sources and/or DSi sinks. This strongly contrasts with available field evidence: BSi was found to be the principal DSi source in leaching water and stream water in different areas [52, 64]. The few studies that have been realized on the reactivity of BSi show complex dissolution rates. Saccone et al.[118] tested different Si extraction techniques and concluded that phytoliths dissolve more easily in alkaline solutions while adsorbed and mineral Si were extractable with acid solutions. The substitution of Si by Al at the surface of BSi particles lowers it reactivity [138]. Loucaides et al. [89] showed a positive correlation between deprotonated silanol (SiO^-) groups, which are present at at the outer surface of phytoliths at pH higher than 2.5-3 and dissolution rates. Given the importance of these processes and and the variable composition of the BSi soil pool (phytoliths of different plant species, testae, spicules,…), it can be assumed that there is a large range of BSi reactivities [129]. Future research should investigate if BSi dissolution is influenced by similar parameters so that eq. 10 may be possibly extended to include BSi dissolution and reprecipitation of this Si as ASi.

2.3. Sinks of DSi

Si is not only released in the water of natural systems but it can also: (1) be adsorbed to soil components; (2) form nanocolloïds by polymerization; (3) take part in neoformation and precipitation as secondary minerals; and (4) actively be precipitated in vegetation as phytoliths.

(1) Monosilicic acid (H_4SiO_4) sorbs on solid phases, mainly on Fe- and Al-oxides and hydroxides. The amount of adsorbed Si increases when pH increases from 4 to 9 [9, 98, 40] and can be quantified with a charge distribution model[70]. Thermodynamically the adsorption can be calculated as:

$$\left(\frac{\delta \log C_{Si-tot}}{\delta pH}\right)_{\Gamma_{Si}} = \left(\frac{\delta \Gamma_H}{\delta \Gamma_{Si}} - n_H\right)_{pH} \equiv (\chi_H - n_H)_{pH} \quad (14)$$

in which $\left(\frac{\delta \log C_{Si-tot}}{\delta pH}\right)_{\Gamma_{Si}}$ is the ratio between the change of the total concentration of DSi ($C_{Si\text{-}tot}$) and the change of pH at a constant silicate loading, Γ_{Si}; $\frac{\delta \Gamma_H}{\delta \Gamma_{Si}}$ is the ratio of change of the proton adsorption over the change of the silicate adsorption; n_H is the proton balance in the solution and χ_H is the proton co-adsorption ratio. Equation 14 implies that the concentration change is equal to the change in H+ adsorption (Γ_H) as result of the adsorption of Si at the surface (Γ_{Si}) at a given constant pH after correction for the mean relative number (n_H) of protons present on the species in solution at that pH. The n_H and Γ_H are calculated for the chosen reference species of DSi, $H_4SiO_4^0$. This is the most common species at pH below 9, which means $n_H = 0$ when the pH <f 9. If $H_3SiO_4^{-1}$ is the only Si species present in significant concentration at pH>9 values n_H will be equal to −1 [71, 114].

(2) Monosilicic acid ($H_4SiO_{4(mono)}$) forms critical nuclei that rapidly develop into nanocolloids ($H_4SiO_{4(nano)}$) by oligomerization. Polymerisation of these oligomers takes place in acidic and neutral environments (2<pH<7). Monosilicic acids are negatively charged at higher alkalinity values. Electrostatic forces then prevent polymerization except when the presence of metal cations allows to neutralize the monomers. If the nanocolloids aggregate or are submitted to processes like coalescence, SiO_2 precipitates [116, 74, 95, 75] and forms ASi particles. Thus, the relative amounts of the different types of Si depend on the environmental conditions. In natural environments, up to 65% of total aqueous silica can be composed of nanocolloïdal silica [27]. High amounts of nanocolloïdal silica are present in environments with low pH (3-4) and at neutral pH in combination with a low ionic strength. In acidic environments the concentration of monomeric Si is in equilibrium with the concentration of nanocolloïdal Si. Si precipitation is rather limited in these conditions in contrast to environments with neutral pH [27]. To simulate the concentrations of monomeric ($[SiO_{2(mono)}]$) and nanocolloïdal SiO_2 ($[SiO_{2(nano)}]$) a supersaturation model (equations 15 and 16) was proposed by Conrad et al. [27]:

$$[SiO_{2(mono)}] = \left(3k_1 t + \frac{1}{\left([SiO_{2(mono)}]_{t=0} - [SiO_{2(eq)}]\right)^3}\right)^{-1/3} + [SiO_{2(eq)}] \quad (15)$$

And:

$$\frac{d[SiO_{2(nano)}]}{dt} = \frac{1}{4}k_1\left[\left(3k_1t + \frac{1}{\left([SiO_{2(mono)}]_{t=0} - [SiO_{2(eq)}]\right)^3}\right)^{-1/3} + [SiO_{2(eq)}]\right]^4 - k_2[SiO_{2(nano)}]^m \quad (16)$$

With $[SiO_{2(eq)}]$ the equilibrium concentration of precipitated amorphous SiO_2, k_1 is the reaction rate constant for the formation of critical nuclei, k_2 is the rate of precipitation and m is the reaction order with respect to $SiO_{2(nano)}$.

(3) Processes of pedogenic formation of secondary minerals (phyllosilicates, silica and short-range ordered aluminosilicates) depend on DSi concentrations in the soil pore water. High Al disponibility favorises clay formation [91]: under these conditions, Short-range ordered Al-Si compounds (hydroxyaluminosilicates, HAS) are formed in soils with pH >5 [144]. HAS are, an amorphous precursor of imogolite [50, 41]. In presence of active organic matter, the formation of allophane and imogolite is suppressed as Al preferentially forms complexes with organic matter in those conditions. As a consequence, opaline silica precipitates (Huang, 1991). It should be kept in mind that for the precipitation of each secondary mineral, specific equilibrium conditions need to be reached.

(4) Plants take up DSi from soil solution especially during the growing season, which can result in a decrease of DSi concentrations during spring and summer [56]. This uptake can be higher (active uptake) than,r proportional to (passive uptake) or lower than (active exclusion) the predicted uptake by water mass transfer. Lower uptake leads to H_4SiO_4 accumulation in the soil. Cornelis et al. [32] reviewed the literature on Si accumulation in plants and showed that both the main source and sink for DSi in soil solutions are phytoliths. Farmer et al.[52] showed that the dissolution of phytoliths stored in soil were the main contributor to DSi in the river water during winter rains and spring snowmelt [52]. However, while there is ample evidence showing that the plant reservoir is important, very little quantitative information is at present available with respect to the relative contribution of biogenic and mineral Si to DSi in soil water for natural and cultural ecosystems. Gérard et al. [63] emphasized this will depend on site-specific conditions.

To calculate the active uptake of Si the Michaëlis-Menten (Monod) rate (equation 17) can be used:

$$r_a = k_M\left(\frac{[Si]}{K_M + [Si]}\right) \quad (17)$$

where r_a is the active uptake of Si (mol $L^{-1}s^{-1}$), k_M is the kinetic constant (mol $L^{-1}s^{-1}$) and K_M is the half saturation constant (mol L^{-1}). This equation is commonly simplified to a first order rate equation (equation 18) by attributing a a very high value to K_M.

For passive uptake r_a is equal to:

$$r_a = \frac{k_M}{K_M}[Si] \quad (18)$$

Which results in a very small value of kM.

Active uptake will lower the Si concentration in soil pore water and the DSi concentration in receiving rivers may therefore be expected to decrease during periods of active DSi uptake by terrestrial vegetation.

2.4. Towards an integrated model

[Fig. 1 about here]

Only a few attempts have been made to simulate the net effect of both sinks and sources on the final DSi concentration in the soil solution and such studies were only carried out for forested environments. Gérard et al. [63] proposed a conceptual model and simulated it using the MIN3P code in which active and passive uptake of Si were integrated. Active uptake was assumed to be important, as there was no evidence for another Si sink.

We propose to estimate the Si concentration by coupling all known equations expressing Si dissolution and sink processes (Fig. 2). Firstly, mineral dissolution in a specific soil horizon is calculated by obtaining r_d from equation 10, which is subsequently by the bulk density (ρ), the porosity (ϕ) and the soil moisture (θ) of the soil horizon under consideration. In the case of active uptake, the uptake by vegetation (described by r_a) has to be accounted for in the root zone using eq. ??.The obtained value (r_{net} in mol L^{-1} s^{-1}) is then multiplied by the duration of a time step (t in s) to obtain the gross increase in DSi concentration, after which losses due to the adsorption/precipitation of Si are estimated using eq. ???. The final Si concentration obtained is the total of the monomeric and nanocolloidal SiO_2. Estimating the relative importance of both fraction requires that the monomeric SiO_2 is measured, e.g. with the molybdenum blue method [73]. Clearly, this Si model needs to be coupled with a water flux model. This is not only necessary to estimate active uptake but also to simulate Si fluxes between different soil horizons.

[Fig. 2 about here]

Fig. 3 is a schematic representation of a podzol soil system to which our model was applied, whereby passive Si uptake by vegetation is assumed. We assumed steady-state downward water flow at a rate of…. As water is flowing downward through the soil profile, the DSi concentration in particular horizon results from the sum of the DSi concentration measured in the horizon above and the produced or deposited DSi in the considered horizon.In general, the simulated DSi concentration builds up with depth (Fig. 3). The relative importance of the parameters (Table 1) from our model (Fig. 2) depend on the active processes in a specific horizon, hence they needed to be estimated for each horizon. Simultaneous mobilization of Si in the humus layer is expected from the processes: dissolution, transfer with upward capillary movement and uptake by roots and mycorrhizal hyphae. Site specific conditions will determine the relative importance of these mechanisms [64].The concentration of organic

363 acids, BSi and pCO_2 (equation 12) are probably most important in the humus layer and in the root
364 zone (A horizon) which should lead to a rapid Si dissolution (Fig. 3). For the humus layer of
365 podzolic soils, low molecular weight organic acids (LMWOA) concentrations ranges between
366 0.50145 mM and 2.6445 mM while pH vary between 2.97 and 3.81 and DSi ranges reach 25-353
367 µM [140].

368 The uptake by vegetation is active in the root zone. In Fig. 3 the relative values of DSi is
369 estimated for a soil with passive uptake by vegetation, the DSi concentration in soil water
370 will not be influenced by vegetation (r_a=0). In the E-horizon most soluble particles have been
371 leached out and only the most stable minerals are left over, which should lead to no further
372 change in DSi concentration in this horizon (Fig. 3). For podzolic soils, LMWOA
373 concentrations ranged from 0.00 to 0.45084 mM, pH from 2.59 to 4.04 and DSi from 103 to 1032
374 µM in the E-horizon. In the B-horizons of these soils, LMWOA concentrations ranged from 0.00
375 to 0.12455 mM, pH from 4.44 to 6.68 [140]. As the acidity is lower in the B-horizon than in the
376 overlying horizons, parameters $\{H^+\}$ and $[org]$ (equation 12) diminish resulting in a lower
377 dissolution rate (r_{d_i} in equation 12) and in generally lower. Resulting DSi concentrations in soil
378 water are generally lower in the B-horizon (116-351 µM in [140]) than in the E-horizon. In the B-
379 horizon DSi can be adsorbed due to the higher concentration of Al- and Fe-hydroxides
380 (equation 16) and oxides and precipitation of secondary minerals can take place (Fig. 3). The
381 concentrations of Al and base cations (equation 12) are probably the most important in the B
382 horizon. To complicate the situation the presence of organic acids, pCO_2 and BSi needs to be
383 accounted for when root zones extent into the E- and B-layers. In that case concentrations of
384 organic acids and BSi will be higher over a deeper section of the soil profile. Finally, DSi
385 concentrations depend on the importance of each of the processes described. In the upper
386 part of the soil profile the poorly known biological and pedogenic processes probably control
387 the Si-cycle.

388 Deeper in the soil, geological processes (weathering of minerals) are controlling the Si-
389 transport. Those processes are better known. In the saturated area, sulfates and carbonates
390 should be taken into account when using equation 12. In Fig. 3, homogeneous bedrock was
391 assumed.

392 [Table 1 about here]

393 Soil moisture will depend on soil texture: θ will typically range between 0.25-0.45 in silt and
394 between 0.1-0.4 in sandy loam. However storage and retention capacities vary through a soil
395 profile: the clay richer B-horizon have a bigger retention capacity which provides a higher θ values
396 [81]. In this horizon residence time (equation 15) of the water will be higher, which gives
397 more time for all processes to take place. In the capillary fringe located just above the
398 groundwater level, θ increases drastically (Fig. 3) and approximates saturation, e.g. ϕ (Table 1).
399 A higher soil moisture will facilitate dissolution as it occurs when water comes in contact
400 with the solid phases of the soil (equation 9, 10 & 11) as well as DSi diffusion from capillary

401 to leaching pore water. The relative water content profile represents an average situation, in
402 dry or wet conditions the top of the profile certainly differs.

403 [Fig. 3 about here]
404
405

406 3. Delivery of Si from the soil to the river

407 The approach to describe DSi mobilization depends on the scale of the study. On a global scale
408 DSi transport depends on lithology and runoff, although vegetation and temperature have been
409 highlighted as potential factors influencing this transport [17, 67,, 79]. This reflects the
410 importance of primary mobilization of Si for the intensity of the Si cycle: even though more and
411 more studies show the importance of the biological pathways, prime mobilization is an important
412 boundary condition for the vegetation and ecosystem filters functioning [129].

413 On the ecosystem scale, general biogeochemical mass balances of Si have been established [15,
414 102]. Processes leading to DSi export are excluded from these models. According to Drever and
415 Stillings [46], transport controls weathering, which process is essentially important in the saturated
416 zone (Fig. 3). Still a lot of different processes appear to influence Si export (Fig. 3). Therefore it is
417 necessary to focus on the different hydrological zones: the unsaturated zone and the saturated
418 zone.

419 The effective transport of the DSi will depend on soil hydraulic parameters like the hydraulic
420 conductivity, the porosity, the bulk density and the matrix tortuosity, dispersivities, effective
421 diffusion coefficient and adsorption partitioning coefficient.

422 Graf and Therrien [66] simulated the transport of DSi with thermohaline groundwater flow at the
423 catchment scale in 3D. Since their focus is on groundwater flow, they only consider saturated
424 (θ=1) conditions and hence neglect plant uptake. They included in their model the effect of
425 adsorption by including a retardation factor. The reactive transport of DSi is expressed in equation
426 18 which assumes fluid incompressibility and constant fluid density[8].

427 $$\frac{\delta(R\phi C)}{\delta t} = \frac{\delta}{\delta x_i}\left(\phi D_{ij}\frac{\delta C}{\delta x_j} - q_i C\right) + \Gamma_m \quad (18)$$

428 In equation 18, i and j are the dimension and equal to 1, 2 or 3, q_i is the Darcy flux (m s^{-1}) which
429 depends on the hydraulic conductivity of the soil, C (kg l^{-3}) is the solute concentration, R [-] is the
430 retardation factor, D_{ij} ($m^2 s^{-1}$) is the coefficient of hydrodynamic dispersion, Γ_m (g l^{-3} s^{-1}) is the
431 source/sink term or the net production of H_4SiO_4. The coefficient of hydrodynamic dispersion D_{ij}
432 is detailed in Bear's equation (equation 19) [8] where α_l (m) and α_t (m) are respectively the
433 longitudinal and transverse dispersivity, τ is the matrix tortuosity, D_d ($m^2 s^{-1}$) is the free-solution
434 diffusion coefficient and δ_{ij} (-) is the Kronecker delta function. The transport will also be retarded
435 partly due to adsorption. The retardation factor R defined in equation 20[55] depends on the bulk

density ρ_b (g m^{-3}) of the porous medium and the equilibrium distribution coefficient K_d (g^{-1} m^3) for a linear Freundlich isotherm.

$$\phi D_{ij} = (\alpha_l - \alpha_t)\frac{q_i q_j}{|q|} + \alpha_t |q| \delta_{ij} + \phi \tau D_d \delta_{ij} \quad (19)$$

$$R = 1 + \frac{\rho_b}{\phi} K_d \quad (20)$$

While Graf and Therrien [66] studied the transport of DSi only for the saturated zone, Gérard et al. [62] investigated processes controlling DSi on the scale of the soil profile, in the unsaturated zone. The DSi concentrations were measured in leachates and in capillary solutions. The seasonality in DSi differed between capillary solutions and leaching solutions, maximum DSi values were observed in different seasons. The DSi concentrations in capillary solutions were mainly controlled by surface weathering. This aqueous Si diffuses then slowly to leaching solutions. Gérard et al. [62] suggest that diffusion goes more rapidly in well drained systems, like those studied by Berner et al.[12]. In Gérard et al. [63]the flux is simulated based on equation 21 through the first 120 cm of a topsoil covered by a forest. In this zone and on this scale the uptake flux (q_p [s^{-1}]) of the solute (C [mol l^{-1} s^{-1}]) by vegetation will have an influence on the Si transport. The soil moisture is also taken into account here as the topsoil is located in the partially saturated zone and since transport can only take place if enough water is available. For the 1D simulation of Si flux through vertical soil profiles, the equation for the hydrodynamic dispersion coefficient D_{ij} (equation 19) has been simplified (equation 22). Retardation is not taken into account in this model since previous research in the same study area pointed out the larger importance of diffusive processes [62].

$$\frac{\delta(\theta\phi C)}{\delta t} = \frac{\delta}{\delta x_i}\left(\theta\phi D_{ij}\frac{\delta C}{\delta x_j} - q_i m\right) + \Gamma_m - q_p C \quad (21)$$

$$D_{ij} = (\alpha_l - \alpha_t) q_i + D_d \quad (22)$$

Here, we showed that the scale of the study and the zone of interest have determined the choice of parameters. To simulate all processes in a catchment we would have to combine equations 18 and 21 and use equation 23. In the partially saturated zone, θ is lower than 1 as opposed to the saturated zone where it is equal to 1. The q_p will be higher than 0 in the root zone in contrast to the zone below the roots where it is equal to 0. For the hydrodynamic dispersion coefficient D_{ij} it is recommended to use equation 19, at least if all parameters can be estimated.

$$\frac{\delta(\theta R\phi C)}{\delta t} = \frac{\delta}{\delta x_i}\left(\theta\phi D_{ij}\frac{\delta C}{\delta x_j} - q_i m\right) + \Gamma_m - q_p C \quad (23)$$

For the soil profile illustrated in Fig. 3, we propose a model as presented in Fig. 4. The DSi is calculated for each soil horizon. The relative importance of the internal processes of each horizon are illustrated by the thickness of the internal arrows. The water flows with the calculated transported concentrations (equation 23) from one horizon to another as illustrated by the dashed arrows. While the saturated zone is assumed to have a homogeneous lithology the DSi

concentrations calculated in the final box should be similar to the DSi concentrations in the river during base flow. Here the transport equation 23 is also used with θ equal to ϕ.

[Figure 4 about Here]

4. External forces altering internal dynamics

4.1. Effect of land use

Land use has an impact on different parameters of the soil-vegetation continuum (soil structure, vegetation, hydrology, etc.) and will impact Si dynamics in ecosystems. Evidently, Si export fluxes from different ecosystems vary significantly [127, 49, 105]. To take into account the role of ecosystem as filter in the Si transport [129], we show for the three most common temperate land use types (croplands, forest and grasslands/pastures) how DSi concentrations and controlling parameters (equation 12) are influenced by land use (Fig. 5). Most research has focused on Si-cycling of tropical and temperate forests [2, 7,56, 63, 26, 22]. Few studies have been realized in grasslands [13, 96, 99] and almost no study [110, 124] deals with Si dynamics in cropland ecosystems.

Weathering rates and the internal biogeochemical cycle of Si depend on the type of vegetal cover (quality and quantity of roots), biomass and litter, which differ from one land cover to another. Plants change soil physical properties by binding fine particles and disintegrating bedrock which alters the surface area and the interaction time between minerals and water. Consequently, chemical weathering rates, root exudates and cation biocycling increase with plant development [84, 10, 4882]. Soil temperature and the susceptibility to erosion depends also on the vegetation cover. Finally, vegetation will have an impact on the chemical properties of the soil solution. The plants and associated microbiota generate chelating ligands and acidifying products like CO_2 and organic acids. Roots take up chemical elements that partly and delayed come back to the soil by degradation of the litter [24, 102, 15, 28, 47, 141]. Hence, land use management will disturb the natural Si-geobiocycling.

Forests have a thick humus layer covering the root penetrated soil profile. Litterfall restitutes large amounts of biologically precipitated Si to the soil system. This implies an increased availability (or large pool) of easily dissolvable Si. Consequently, DSi concentrations are high (last column of Fig. 5), e.g. 375±126µM in soil water and 423±52 µM in river water at base flow [23]. Forests soils are typically acidic but still differ between tree-stand compositions, e.g. pH is lower in coniferous forests than in deciduous forests (Johansson et al., 2003). The thick humus layer will also provide organic acids and dissolved organic matter to the soil solution[111], which enhances the dissolution of Si (equation 12). Moreover, uptake of DSi is quite important, although it is not proven that this is an active process in forests [31]: r_A was thus neglected for forests in Fig. 5. In comparison to their DSi losses, forests are characterized by an important internal biogeochemical (re-)cycling of Si [2, 91,100]. In temperate forests, vegetation uptake ranges from 2.3 to 43 kg ha^{-1} yr^{-1}, Si restitution by litterfall ranges from 2.1 to 41 kg ha^{-1} yr^{-1}, while the export by drainage from

507 the catchments ranges only from 0.7 until 28 kg ha^{-1} yr^{-1} [7, 30, 97, 63]. Due to this intensive
508 internal cycling, the transport of DSi towards the river is delayed [25]. BSi preservation in forest
509 soils has been shown for different climates, the stable BSi pool represents an accumulation rate 4
510 to 6 kg Si $ha^{-1}yr^{-1}$ in equatorial rainforests [2] and 0-1 kg Si $ha^{-1}yr^{-1}$ [7] in temperate deciduous and
511 coniferous forest. Weight percentages of ASi determined for a forest soil reached 0.5-1.4% in the
512 humus layer (pH 3.8), 0.3-0.6% in the topsoil and 0.3-0.4% at 30 to 45 cm depth (pH 4.5). Soil
513 water from topsoil had a pH of 4.12-5.05 and concentrations of dissolved organic carbon of 23.5-
514 69.0 mg/l resulting in DSi concentrations of 30.6-64.5 µM. At 60 cm depth, soil water had a pH of
515 4.75-5.52 and concentrations of dissolved organic carbon of 2.3-3.7 mg/l resulting in DSi
516 concentrations of 60.2-80.8 µM at 60 cm depth [29]. Fig. 5 illustrates similar trends trough the soil
517 profile: a parallel decrease for ASi and organic acids as well as an increase of pH and DSi with
518 depth.

519 Soil profiles of grasslands are characterized by shallow roots and a humus layer. Grasses
520 accumulate Si actively, this means Si uptake is larger than water uptake [92]. The biological Si
521 cycling in grasslands is more or less comparable with the biocycling of forests. However, the Si
522 biocycling has greater impact on mineral weathering in grasslands than in forests [13]. The amount
523 of soil phytoliths diminishes like soil organic C with depth (Fig. 5). Blecker et al.[13] measured in
524 different topsoils 0.2-0.5 g cm^{-2} soil organic C and 0.1-0.5 g cm^{-2} phytoliths. For the same soils at
525 70 cm depth, both parameters were $\leq$0.1 g cm^{-2}. The storage of BSi in grassland soils is relatively
526 high compared to forests and varies from 4 to 16 kg Si $ha^{-1}yr^{-1}$. Different causes have been
527 proposed for this relatively low bio recycling. Climatic weathering could be more important in
528 forests enhancing dissolution processes [13]. The lower specific surface of phytoliths could also
529 explain the lower solubility (10-15 times) of grass BSi in comparison to forest BSi[148]. Due to
530 intensive mowing, and possibly cattle grazing of grasslands, a part of the BSi pool is removed
531 from the ecosystem [127]. In this case, the ASi accumulation in the soil will not be replenished (or
532 restituted) by plant uptake, which could eventually result in depletion of easy dissolvable Si pool.
533 In contrast it has also been shown that grazing can lead to higher BSi in grasses [96, 99].
534 Resulting DSi concentrations in natural waters are rather low compared with forest (last column in
535 Fig. 6), e.g. 108±50µM in soil water and 183±37µM in river water [23].

536 In croplands, harvesting, erosion and the use of fertilizers can lead to Si-depletion in soils. For
537 some specific tillage technique, roots are only present in growing season and are absent during
538 winters due to harvesting. Harvesting prevents litter accumulation and the development of a humus
539 layer which leads to low BSi accumulation in cropland soils [101,; 110, 139]. Erosion is important
540 in croplands as bare soils are exposed to the wind and precipitation. Soil erosion can be especially
541 high during peak-events leading to the removal of ASi from the soil. As a result, dynamics of DSi
542 and ASi in river water of cultivated first-order catchments differ between peak flow events and
543 baseflow[124]. Resulting DSi concentrations in soil water are rather low, e.g. 106±41 µM and
544 204±63µM for different sites[23]. The use of nitrate fertilizers enhances the weathering of Si as
545 nitrification processes releases acids[53].

546 Fig. 5 summarizes the general processes influencing the DSi concentrations for each type of land
547 use. Soil temperature is generally lower under forest than under grassland cover. Cropland soils
548 have higher temperatures and seasonal variations are more important compared to the other land
549 uses [135, 120]. As the measured temperature differences between cropland, grassland and forests
550 are in the order of magnitude of a few degrees (°C), these differences will probably not influence
551 directly the dissolution of Si but can influence biological activity and thus the uptake of DSi, the
552 amount of organic acids, pCO_2, etc. In general the pH is lower in forests than in grasslands and
553 arable lands. The amount of dissolved organic matter is the highest in forests and lower in
554 croplands than in grasslands. The pCO_2 in soils was proved to be the highest in arable land,
555 followed by grasslands and lowest in forests [1]. The acidity parameters (equation 12) driving
556 dissolution are thus different following the land use: in forests organic acids and pH are important
557 but in grassland and cropland pCO2 will be more important compared to forests.

558

559 [Fig. 5 about here]

560 ## 4.2. Seasonal climatic variation

561 Seasonal variations of DSi have been observed in water of temperate forested catchments with
562 humid winters and dry summers ([88, 105]. In summer, rainfall events are typically more
563 intensive. Various explanations are given for the temporal variation in DSi transport [113, 56,105].
564 If lithology of the aquifer varies vertically, more weatherable layers can be in contact with high
565 groundwater levels and release Si, in which case water chemistry can be correlated with
566 groundwater level [113]. The decrease of DSi in natural waters during the growing season can be
567 explained by the DSi uptake by vegetation [56] or by the consumption of DSi by diatoms in the
568 river [105]. In the first case the decrease will be observed in soil waters in contrast to the second
569 case were the decrease is only observed in river water. Gérard et al. [62] observed a significant
570 seasonal variation in soil water and connectivity between the soil and river system: DSi
571 concentrations in capillary soil solutions were generally ca 35 µM lower during winter than during
572 summer.
573 The autumn-winter period characterized by:
574 - low evapotranspiration rates which induces low uptake of DSi by passive vegetation,
575 illustrated by a weak interaction for forest and grassland or no interaction in cropland in
576 Fig. 6;
577 - higher soil moistures (θ in Fig. 6) and groundwater levels which can enhance dissolution
578 of the lithologies (equations 9, 10, 11);
579 - decaying organic matter releasing BSi into the soil giving a larger fresh ASi stock
580 available, especially in forests where litterfall is important (BSi in Fig. 6);
581 - polymerization of DSi and complexation of Si with particulate material when water
582 freezes [133].
583 During spring and summer, other processes are important:

- higher evapotranspiration rates, which induces dryer soils and higher uptake of DSi by vegetation, illustrated as important interaction in Fig. 6 ;
- lower soil moistures (θ in Fig. 6) and lower groundwater levels (equations 9,10, 11) limiting unsaturated transport of DSi to the aquifer [23];
- higher temperatures increases biological activity which leads to more acid production (pH or H^+, [org] and pCO_2 in Fig. 6 and equations 6, 7, 8 & 12);
- higher acid production results in Si desorption and in a shift of cation exchange equilibria, i.e. base cations are replaced by H^+ on the mineral surfaces (equations 6, 7, 8 & 12) [12].

To conclude, DSi concentrations should generally be lower during winter than during summer as acid production will drive a lot of processes enhancing Si dissolution. Transport processes in the dry summer will be slower: maximal DSi concentrations can be observed at different times in soil capillary soil water, leaching solution and river water due to diffusion processes from capillary to leaching solution [62] or due to a long transport time from soil to river.

[Fig. 6 about here]

5. Discussion and conclusions

This review presents a conceptual model for DSi transport from landsurface, through each soil horizon of a typical podzol soil, subsurface until the river for catchments with temperate climate. This is the first time a framework of equations is proposed that may be used as a first step to develop a mechanistic model for DSi production and transport. The proposed model needs to be validated by applying the model on fields. As each field has its own specific characteristics, the user of such an equation framework can check which controlling processes and rate limiting processes are important in his study case. Based on that analyse the user can simplify the framework by dismissing some processes, if needed. Still several unknowns need to be further clarified to entirely understand the Si-cycle. On the scale of the soil profile, not all pedogenic processes are known. The influence of sulfates in the saturated zone have been observed in some study cases [83,87] and should be better studied to determine if it is an important process or not. The influence of microbial activity on mineral changes seems difficult to quantify. The reactivity of BSi particles in soil profiles have not been well studied, i.e. is BSi reacting like mineral Si to pH changes?

By analyzing the parameters driving DSi production (equation 12), we could state seasonal variation of DSi export is linked to the importance of biological activity. Si-cycling is more important during spring and summer due to high biological activity inducing for example higher acidity production. This results in lower DSi concentrations in soil water during autumn and winter compared to spring and summer.

The BSi storage, the Si-cycling and Si-export differs for the three types of land uses (forest, cropland, grassland). It results in high DSi concentrations in the forest rivers. Following the analysis of controlling parameters (section 4.1.), relatively high concentrations are expected in

grasslands and low concentrations in croplands due to the respectively decreasing BSi storage and soil acidity. Nevertheless the data from Clymans [23] show no significant difference between DSi in soil water of grassland and cropland. Moreover, the comparison of soil water DSi in different catchments with the same land use [23]show different DSi concentrations. This emphasizes the importance of determining the site-specific parameters influencing the Si transport. On the catchment scale, we emphasized that ecosystem management has an impact on the Si cycle. It is not clear in grazed grasslands how the digestion of grasses influences the availability of BSi to the Si-cycle. Deforestation, harvesting, mowing, grazing retrieve BSi stored in vegetation from the specific ecosystems (forest, cropland or grassland). However the destination of BSi retrieved by deforestation, harvesting and mowing is unknown, it might be released in another Si cycle or not. This is important to figure out for Si-budget calculations on a large scale. However, some parameters (i.e. soil water content, base cations) of our dissolution model are sometimes difficult to compare from one land use type to another as they are influenced by site specific factors (meteorological conditions, soil mineralogy).

Struyf et al. [127] proposes a model for the evolution of the Si-cycle and the Si transport during baseflow due to land-use changes. This model proposes an increase in DSi export during the development of a forest, a relatively constant and high export during the climax phase of the forest development. The deforestation will induce a quick increase of Si export [88, 6, 26] on the short term (<20yrs; [26]). Likens et al. [88] supposed the deforestation increased the weathering of primary minerals, but knowing that ASi is much more soluble than primary silicates, Conley et al.[26] proposed three other hypotheses. The excess of DSi can result from the dissolution of ASi contained in cut vegetation left on the soil. Another possible explanation is the mobilization of the large amount of BSi stored in forest soils[25, 13]. The last hypothesis to explain the excess of DSi exported after deforestation is an enhanced leaching due to the re-establishment of vegetation. As the ASi amount diminishes after deforestation the long term evolution (500-1000 yrs; 127] of landscapes from forest to cropland would generate on the long term a diminishing Si export. Clymans et al. [22] observed that historical land use changes resulted in a 50% decrease of BSi storage in Swedish soils. This diminishing Si export can be explained by the change in chemical and physical properties of soils thus by the change in dissolution driving parameters (equation 12). Even if the pH will increase when forest becomes cropland or pasture, the base exchange properties will increase. This could have a lowering effect on DSi concentrations of soil water. Moreover, the decreasing porosity will diminish infiltration capacity and increase erodability [51, 117]. As erodability increases, BSi depletion of soils will start.

An important question remains: how much DSi exported from out of a catchment comes from BSi relatively to MSi? To understand the relative contribution of the biological filter to eventual output of DSi, Derry et al.[34] combined Ge/Si ratios with the Si concentrations. Cornelis et al. [32]recommended to make a Si mass balance and combine the use of Ge/Si and δ^{30}Si as geochemical tracers. These tracers can be used because they are fractionated during the biogeochemical cycle which implies that different sources have different tracer's signatures [109]. Germanium concentrations are relatively high in clayey weathering products compared to

661 concentrations measured in phytoliths [104, 86, 121, 14,33]. The light Si isotopes are
662 preferentially built-in secondary clay minerals, taken up by plants and adsorbed on Fe-oxides. Due
663 to this processes the DSi flowing into the river will be enriched in heavy isotopes [110, 29, 42, 18,
664 36, 35, 60,61] . Si isotopes and element ratios (Si/Mg; Ge/Si) can be good proxies to understand
665 which processes (weathering, uptake by diatoms, uptake by terrestrial vegetation) influence the
666 seasonal variation of DSi in river water [49, 32]. Using these two elements has several advantages:
667 the ratio Ge/Si can be related to the geochemical source of Si and hence sources with similar Si
668 concentration can be differentiated. All these approaches are still in early stages of development,
669 therefore it is presently difficult to assess different Si sources based on either method. Early results
670 are mainly related to small scale isotope fractionation in isolated soil-plant systems, for few
671 species only (Musa sp., bamboo, …). On the catchment scale, isotope signatures are still difficult
672 to assign, as different biogeochemical mechanisms contribute similarly to isotope ratios. More
673 detailed research on these tracers in specific land use types could significantly enhance this
674 research.
675
676 To assess CO_2 consuming processes like Si weathering [20] or diatom uptake, the exact
677 quantification of the total amount of Si in soils and total amount of DSi transported from the
678 continent to the ocean are essential. In contrast to our proposed model, current approaches
679 (e.g.[65]) ignore the biogenic Si pool as a DSi source, DSi sinks like Si uptake by plants or Si
680 nucleation and differences due to the land use types. Prediction models of global DSi transport in
681 the future will have to take these factors into account as well as the expansion of agriculture
682 (Gordon et al., 2008) and the rising number of peak events due to climate change. Transport of
683 DSi from soil to river will probably diminish in the future. In this study only three land uses were
684 analysed. In urban areas, the Si transport needs to be tackled in a different way, anthropogenic
685 point sources (industries) need to be taken into account and as exposed soil is rather scarce, raw
686 materials will be sources of Si during runoff events [123].

687 To tackle the eutrophication problem the Si:N:P ratios should be considered in order to obtain the
688 whole picture. Eutrophication is due to increasing N and P concentrations, while Si concentrations
689 would not change [21]. Snowmelt periods need to be analysed carefully as DSi can be diluted in
690 rivers during snowmelt periods while nitrates increase enhance eutrophication [68, 69, 149). Since
691 we discussed the shifts of DSi transport by land-use changes and these changes can affect also the
692 leaching of N [51], the impact of land use changes on the Si:N:P should be further analysed.

693

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701

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Fig.1: Classification of Si compounds present in soils. Arrows show increasing stability of solid compounds against weathering (Sauer et al., 2006; Cornelis et al., 2011).

Fig. 2: Estimation procedure for Si concentration in soil water and groundwater by taking into account dissolution and sink processes. This model is based on equations 10, 14, 16 and 17.

Fig. 3: Typical soil profile in temperate climate. Processes and soil moisture vary with depth from one horizon to another. DSi relative values are estimated for this soil covered by vegetation with a passive uptake of Si and with important adsorption and precipitation processes in the B horizon.

Fig. 4: Conceptual model of the transport of DSi through each horizon. Each box is an horizon with dissolution and sink processes of different relative importance (thick arrow: important process). Dashed arrows show the transport from one horizon to another, until the river as final receptor.

Fig. 5: Relative importance of the parameters (BSi, [org], pCO2, pH, $[SO_4^{2-}]$,$[CO_3^{2-}]$,θ, r_A) influencing the DSi concentrations in natural waters of forests (F), grasslands (G) and croplands (C); parameters influence equations 10 and 12.

Fig. 6: Processes influencing the DSi dissolution in soils of forests, croplands and grasslands during summer and winter, assuming the same soil type for the three cases.

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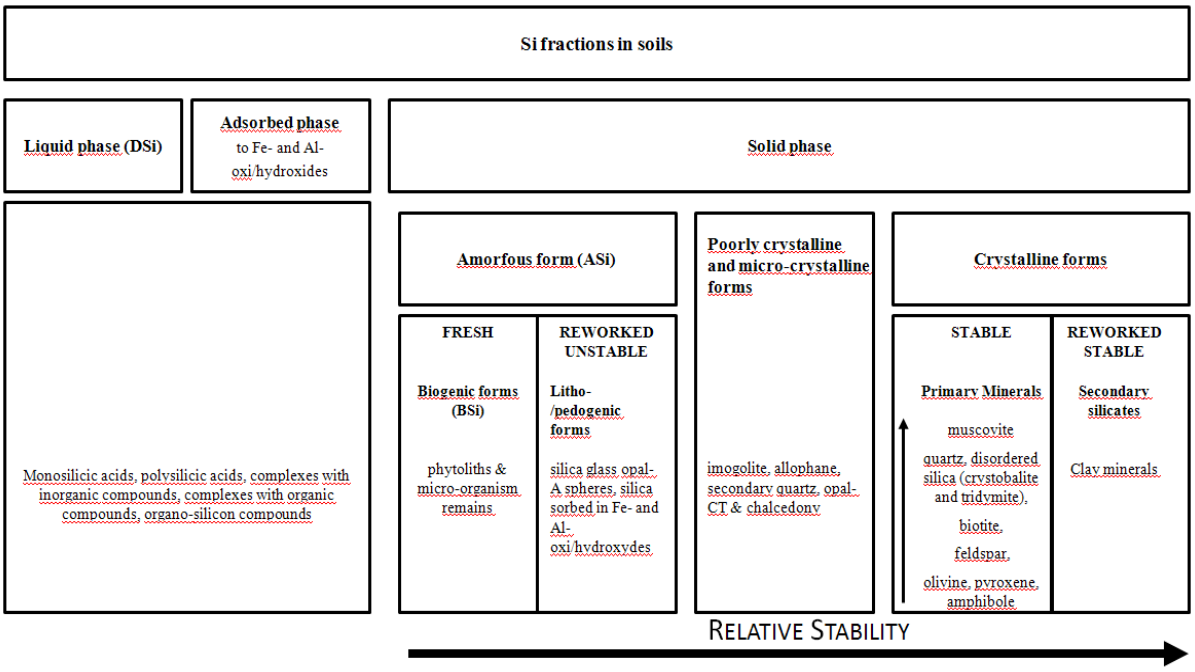

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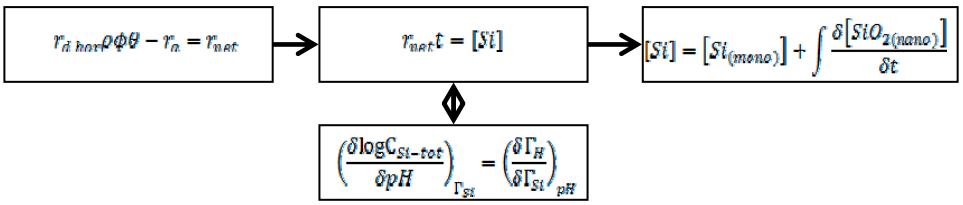

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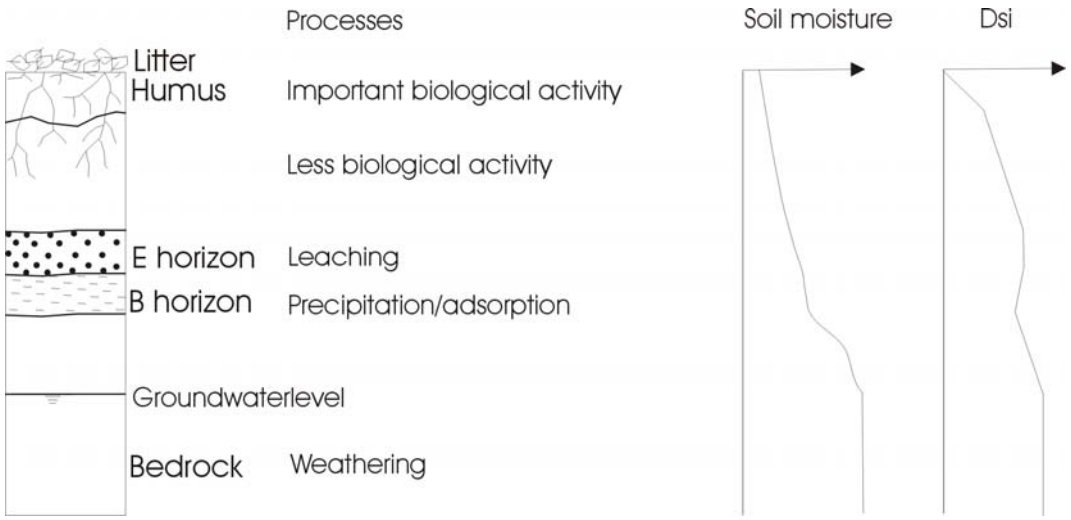

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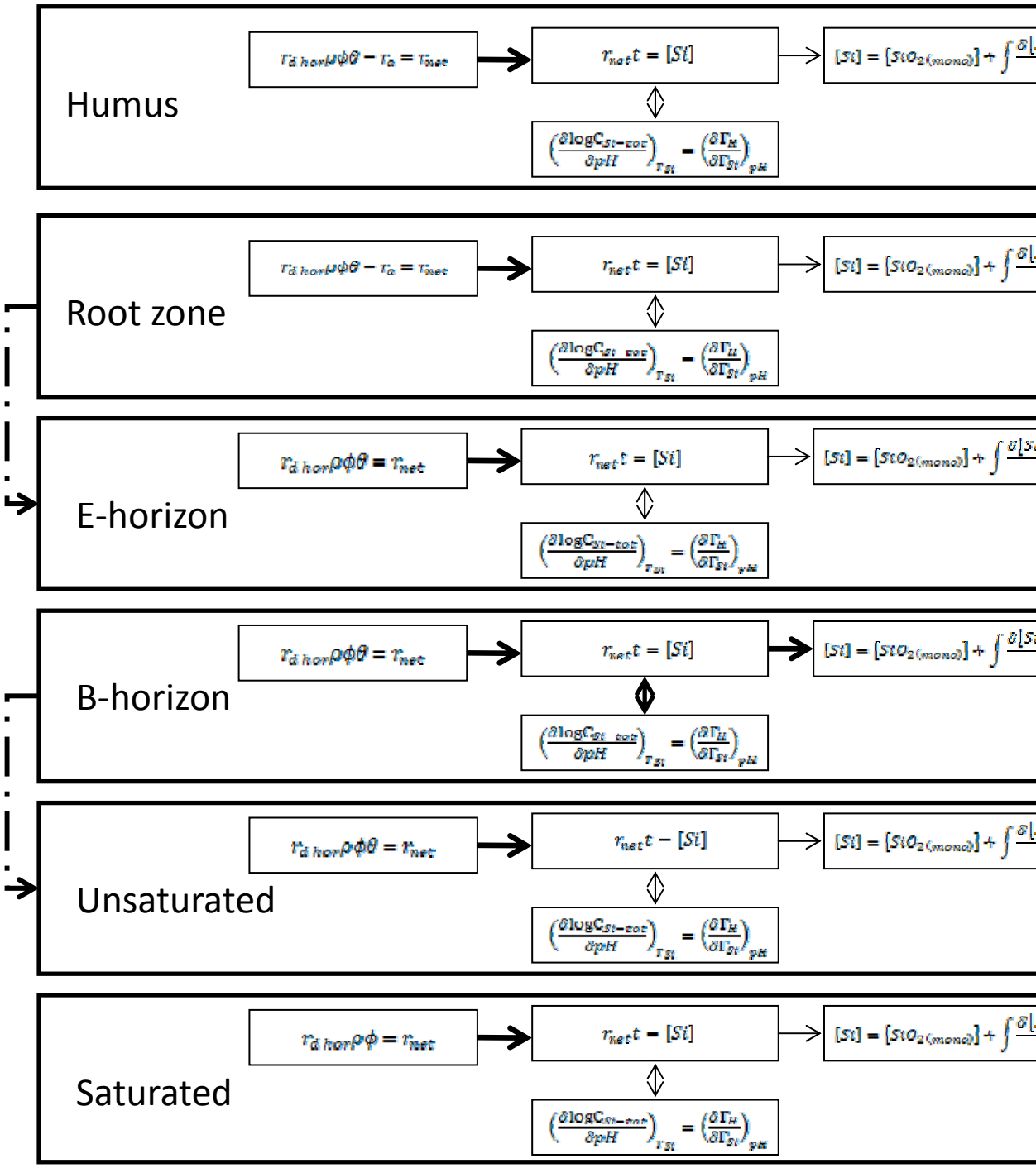

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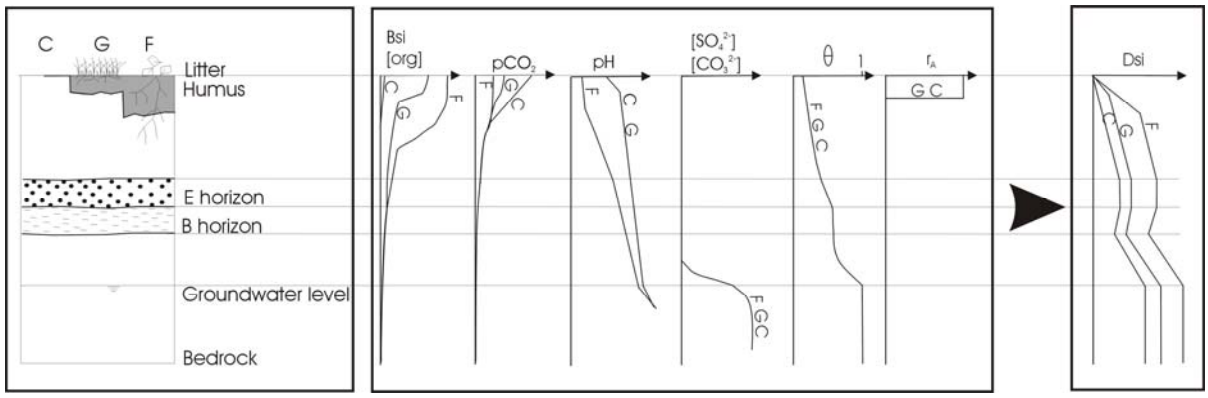
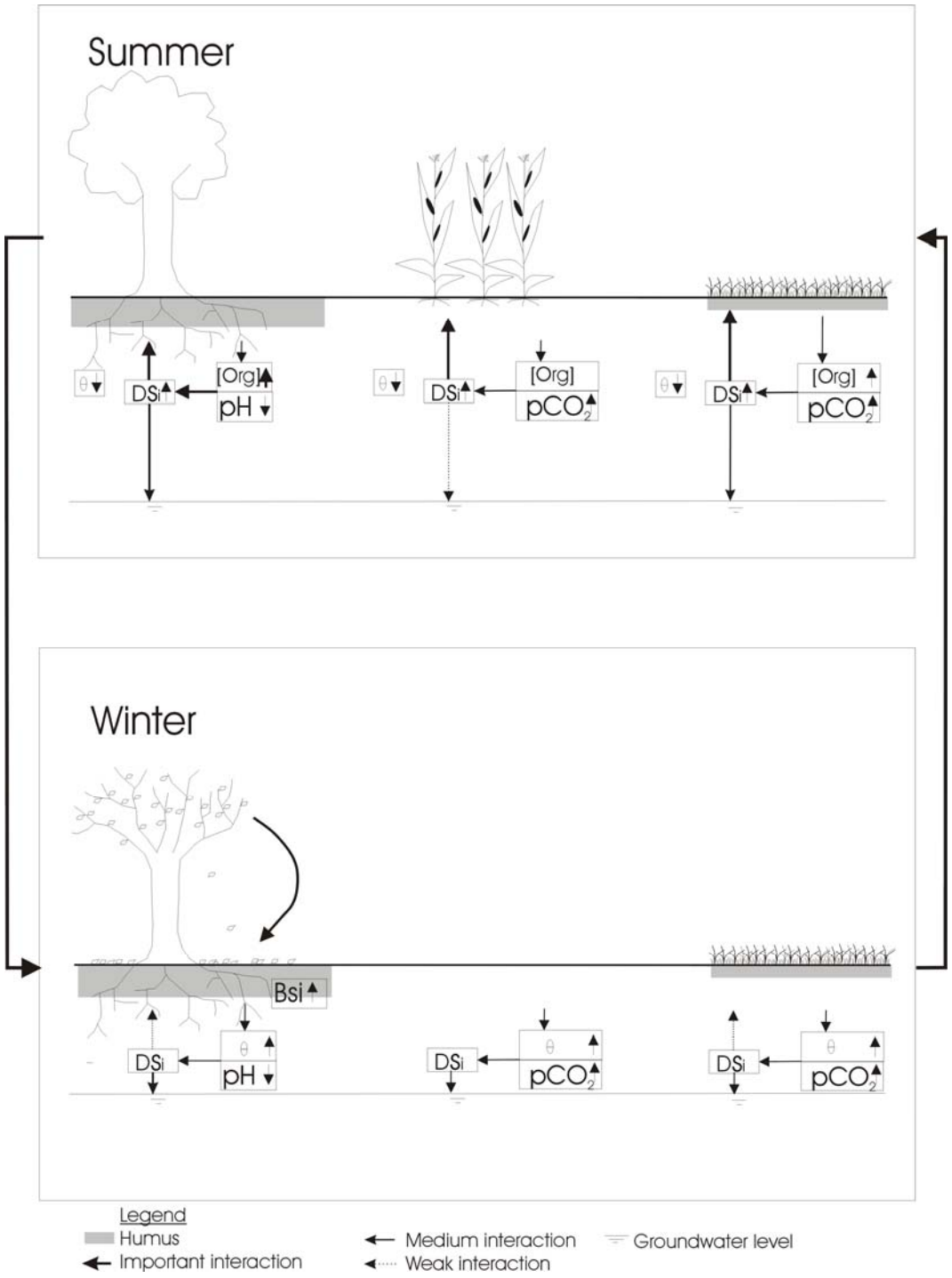


Fig. 5: Relative importance of the parameters (BSi, [org], pCO2, pH, $[SO_4^{2-}]$,$[CO_3^{2-}]$,θ, r_A) influencing the DSi concentrations in natural waters of forests (F), grasslands (G) and croplands (C); parameters influence equations 10 and 12.



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1136 **Fig. 6**: Processes influencing the DSi dissolution in soils of forests, croplands and grasslands
1137 during summer and winter, assuming the same soil type for the three cases.

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List of Table Captions

Table 1: Relative importance of parameters of equations 10, 12 and 17 for each soil horizon for a soil profile like presented in Fig. 3. +++, ++, +, ±, - is the scale from very important to unimportant. 0 stands for negligible and ϕ for porosity.

List of Tables

Table 1: Relative importance of parameters of equations 10, 12 and 17 for each soil horizon for a soil profile like presented in Figure 3. +++, ++, +, ±, - is the scale from very important to unimportant. 0 stands for negligible and ϕ for porosity.

		r_d					θ	r_a[1]
		$[H+]$[1]	$[CO_2]$[1]	$[org]$[1]	$[SO_4^{2-}]$	$[CO_3^{2-}]$		
Unsaturated	Humus	+++	+++	+++	0	0	$< \phi$	±
	A horizon	++	++	++	0	0	$< \phi$	±
	E-horizon	+	+	±	0	0	$< \phi$	0
	B-horizon	-	±	±	0	0	$< \phi$	0
Saturated zone		±	±	±	±	±	ϕ	0

[1]This factor needs to be taken into account if uptake is active and only in the root zone.

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