

This item is the archived peer-reviewed author-version of:

Factors controlling Si export from soils : a soil column approach

Reference:

Ronchi Benedicta, Barão Lúcia, Clymans Wim, Vandevenne Floor, Batelaan Okke, Govers Gerard, Struyf Eric, Dassargues Alain.- Factors controlling Si export from soils : a soil column approach
Catena: an interdisciplinary journal of geomorphology, hydrology, pedology - ISSN 0341-8162 - 133(2015), p. 85-96
DOI: <http://dx.doi.org/doi:10.1016/j.catena.2015.05.007>

1 **Factors controlling Si export from soils: a soil column approach**

2 Ronchi Benedicta^{1*}, Barão Lúcia², Clymans Wim³, Vandevenne Floor², Batelaan Okke⁴, Gerard
3 Govers¹, Eric Struyf², Dassargues Alain⁵

4 ¹ KU Leuven, Department of Earth and Environmental Sciences, Celestijnenlaan 200 E, 3001 Leuven,
5 Belgium

6 ² University of Antwerp, Department of Biology, Universiteitsplein 1C, 2610 Wilrijk, Belgium

7 ³ Lund University, Department of Geology Sölvegatan 12, 223 62 Lund, Sweden

8 ⁴ Flinders University, School of the Environment, GPO Box 2100, Adelaide SA 5001, Australia

9 ⁵ Université de Liège, Hydrogeology and Environmental Geology, Department of Architecture,
10 Geology, Environment, and Civil Engineering (ArGEnCo), B.52/3 Sart-Tilman, 4000 Liège, Belgium

11 *benedicta.ronchi@gmail.com

12 *Abstract*

13 *The release of dissolved silicon (DSi) from A and B horizons was investigated with leaching tests on*
14 *unsaturated columns. As forest A horizons have larger biogenic Si (BSi) pools than arable lands, we*
15 *compared the Si release from a forest and a cropland from the same geographical region developed*
16 *on a Luvisol in Belgium and a Cambisol in Sweden. The A horizons released a quickly dissolving Si*
17 *fraction in contrast to the B horizons, which did contain no or only little amounts of BSi and released*
18 *lower Si concentrations. Our experiments show that Si export from forest soils is high because of the*
19 *presence of a large reservoir of soluble BSi as well as due to the acidity of the soil (pH < 4). Leaching*
20 *at two different water fluxes revealed that export in forest soils was transport controlled while*
21 *cropland soils were in equilibrium.*

22 *Keywords: biogenic Si; pedogenic Si; reactivity; flux; land use*

23 1. Introduction

24 Dissolved Si export from terrestrial catchments has long been thought to be fully controlled by
25 chemical weathering processes (Garrels and Mackenzie 1967). However, it is now clear that the
26 dissolution of soluble, non-crystalline silica particles present in soils does affect Si export (Derry et al.
27 2005; Sommer et al. 2006; Street-perrott and Barker 2008). Part of this non-crystalline Si is of
28 biological origin (BSi). BSi is formed when dissolved Si, primarily derived from the weathering of
29 silicate minerals, passes through plants which form phytoliths. The presence of a BSi reservoir affects
30 Si cycling in soils. The dissolution of non-crystalline Si is controlled by the same chemical soil water
31 parameters (pH, base cations (BC)) controlling the dissolution of silicates (Dove 1995; Dove et al.
32 2008) but experiments have shown that BSi solubility (1.8 mM Si) can be up to 17 times higher than
33 that of quartz (0.10–0.25mM Si) (Frayse et al. 2006). The BSi solubility varies depending on the Si/Al
34 ratio, the surface area of the BSi and the water content of the soil (Bartoli and Wilding 1980; Bartoli
35 1985), as well as phytolith morphology and association with organic matter (Watteau and Villemin
36 2001). The accumulation of BSi in the terrestrial realm modulates the final Si export from the land to
37 the ocean. As terrestrial ecosystems have been heavily disturbed by human activities over the last
38 centuries, the steady-state principle of Si delivery towards oceans is now being questioned (Frings et
39 al. 2014). This concept has become known as the “ecosystem Si filter” (Struyf and Conley 2012).

40 Biogenic Si is not the only form of non-crystalline Si present in soils. Dissolved Si flowing through the
41 soil profile, can also reprecipitate as amorphous or poorly crystalline Si phases (Chadwick et al. 1987;
42 Doucet et al. 2001) recognized as precursors for secondary clays (Dixon et al. 1989), or adsorb on Al-
43 and Fe-(hydr)oxides deeper in the soil profile (Beckwith and Reeve 1963; McKeague and Cline 1963).
44 These fractions are grouped under the name “pedogenic Si” (PSi). This PSi fraction occurs typically in
45 deeper soil layers, and appears to be more reactive than BSi during alkaline extraction experiments
46 (Barão et al. 2014). Outside the lab environment little data is available on the solubility of the PSi
47 fraction in soils and the importance of its contribution to the Si export towards rivers. White et al.

48 (2012) used Ge:Si ratios to trace controls on pore-water Si levels. They suggested a seasonal control
49 of P_{Si} on pore-water D_{Si} levels through the formation and dissolution of poorly-crystalline Si
50 fractions, exemplifying its potential importance. The total quantity of both types of Si combined (B_{Si}
51 and P_{Si}) can be measured through alkaline extraction (DeMaster 1981; Sauer et al. 2006). We will
52 refer to it using its procedural term: alkaline extractable Si (AlkExSi) as proposed by Barão et al.
53 (2014).

54 Silicate weathering reactions consume CO₂ from the atmosphere and convert it to bicarbonate in
55 river and groundwater (Cochran and Berner 1996; Lucas 2001). The chemical composition of natural
56 water, particularly its D_{Si} concentration, is therefore often considered as a good indicator of the
57 mineral weathering rate (Garrels and Mackenzie 1967; Oliva et al. 2003). Plants are recognised to
58 change soil physical properties by binding fine particles and disintegrating bedrock, which
59 consequently changes surface areas and enhances silicate weathering (Drever 1994). They also
60 generate weathering agents such as acidic organic root exudates and recycle soluble cations (Kelly et
61 al. 1998) and affect soil pH by producing H⁺-protons and CO₂ (Hinsinger et al. 2001). Cochran & Berner
62 (1996) demonstrated that chemical denudation rates for basalt covered by plants were ten times
63 higher than for bare basalts, which were only colonized by microbial communities. Experiments
64 showed that the presence of plants on basaltic rock could increase the release rates of Si by a factor
65 of 2 (Hinsinger et al. 2001). Field weathering rates were two and three times higher for soils
66 respectively covered with birch and conifers than for bare soils (Moulton et al. 2000).

67 However, silicate weathering is not only surface reaction controlled. Maher (2010) suggested that
68 weathering in most granitic sediments is transport-controlled, i.e. dependent of fluid residence time
69 and fluid flow rates. Dominant factors in transport-controlled weathering are fluid flow, pH and
70 mineral solubility, whereas surface area and mineral kinetics are less important (Maher 2010). Plant
71 root distribution determines water uptake (Jackson et al. 2000) from the soil and thereby affects the

72 importance of different flowpaths and water residence time. Consequently, a change in vegetation
73 may also impact transport-controlled weathering.

74 Given the strong interactions between plants and the Si cycle, it can be expected that land use
75 changes such as deforestation can significantly alter catchment scale Si fluxes, a hypothesis which
76 was confirmed by recent empirical studies (Conley 2002; Carey and Fulweiler 2011). Struyf et al.
77 (2010) found a positive relationship between the presence of forests in a catchment and DSi export.
78 In their conceptual model, they introduced, alongside the above described effects on weathering,
79 also the potential role of a larger AlkExSi (BSi+PSi) pool in forested systems as a source for enhanced
80 Si delivery. In their model, the initial rapid leaching of the present AlkExSi pool increases Si delivery in
81 the first decennia following deforestation, but over a centennial scale the reduced BSi replenishment
82 due to crop harvesting leads to a lowered Si delivery (Vandevenne et al. 2012; Keller et al. 2012). The
83 alteration of Si fluxes from the land to the water after deforestation or land use change may not only
84 have significant effects on the productivity and composition of aquatic ecosystems but may also
85 affect the biological CO₂ pump in the oceans. The latter is directly related to the ocean's primary
86 productivity, which is strongly controlled by Si consuming plankton, i.e. diatoms (Conley et al. 2008;
87 Laruelle et al. 2009; Struyf et al. 2010; Carey and Fulweiler 2011).

88 Although several studies have confirmed that the size of AlkExSi pool in soils depends on land use
89 and land management (Clymans et al 2011, Guntzer et al 2011, Keller et al 2012, Vandevenne et al
90 2012), few studies so far focused on the role of the different fractions in the AlkExSi pool in soils in
91 controlling the actual Si release (Cornelis et al 2010, Cornelis et al 2014, White et al. 2012). Pore-
92 water samples collected in the field can only be used to a limited extent to assess controls on AlkExSi
93 solubility. First, it is hard to control the complexity of the natural hydrological system in the field as
94 water fluxes, pore water chemistry, and more specifically pH and chemical saturation state, can vary
95 locally (Neal 1997) due to soil heterogeneity and vadose zone processes (Neal 1996). Secondly, while

96 DSi concentrations can effectively be measured, it is much more difficult to determine the
97 contribution of the different possible sources to the total DSi flux.

98 Laboratory column studies can overcome these objections to some degree as water fluxes and water
99 composition can be controlled for different horizons separated in different columns. Thus, one can
100 gain insight in the origin of the DSi. The aim of this study is to use such column studies (i) to test the
101 hypothesis that the size of the AlkExSi pool, here coincident with the land use component, influences
102 Si release, and (ii) to assess the contribution of BSi and P_{Si} dissolution to the Si export. We performed
103 leaching experiments on soil samples from the A and B horizons (to investigate the effect of the
104 AlkExSi pool composition) collected at a forest and arable site (to investigate the effect of the size of
105 the AlkExSi pool). The samples were collected from two land use gradients with contrasting parent
106 material to explore the reproducibility of results: Luvisols developed on loess from Belgium, and
107 Cambisols developed in glacial till overlaying a granite bedrock from Sweden. Thus, this study is a
108 first step to verify the validity of the hypothesis that Si delivery depends on the size and speciation of
109 the AlkExSi pool in soils.

110 **2. Material and methods**

111 *2.1. Study sites and background data*

112 Our study used soil samples from two land use gradients developed on different parent materials in
113 temperate regions. The first location is in the Belgian Loam Belt and has a temperate climate with
114 long-term mean annual precipitation of about 760 mm and a mean January and July temperature
115 lying respectively between 3°C and 4°C and between 17°C and 18°C. Samples were collected from
116 hillslopes in a catchment under forested (Meerdaal forest, f_{iv} site, 50°48'N, 4°40'E) and in a
117 catchment under high-intensity arable land use (Ganspoel, c_{iv} site, 50°48'N, 4°35'E) (Vandevenne and
118 Barão *et al. submitted*). Soils in both catchments were Luvisols developed on eolian loess deposits
119 (Van Ranst *et al* 1982). *Soil pits were dug for soil sampling per horizon while samples for analysis were*
120 *taken by coring (Table 1 and 2, Vandevenne and Barão *et al. submitted*).*

121 In Sweden, samples were taken through coring in a catchment under continuous forest (Siggaboda,
122 f_{cb} site, 56°27'N, 14°12'E) as well as one under arable land use (Råshult, c_{cb} site, 56°36'N, 14°11'E)
123 (Clymans et al. 2011, Barão et al. 2014). This agricultural site is different from the Belgian site as it is
124 located in a cultural reserve where traditional, low-intensity tillage (without chemical fertilization) is
125 practiced and a two to three year ley is used between crops. Agricultural intensity at Råshult is
126 therefore clearly lower in comparison to the Ganspoel site. The mean annual precipitation is ca. 700
127 mm yr⁻¹ and January and July temperature vary respectively between -2°C and -3°C and between
128 15°C and 16°C. The Swedish soils developed on sandy till underlain by granitic bedrock and were
129 classified as Cambisols. The Cambisol soil samples were collected through coring in flat areas. A
130 detailed description of the study area and the sampling technique was presented in Clymans et al.
131 (2011). Soil samples used for our experiment came from a replica taken next to the corings used for
132 soil analysis (Table 1 and 2, Clymans et al. 2011, Barão et al. 2014). Throughout the study we
133 indicated our sites with acronyms (f_{lv} , c_{lv} for the forested and cropland site on Luvisol in Belgium and
134 f_{cb} , c_{cb} for the forested and cropland site on Cambisol in Sweden, respectively), specific horizons are
135 indicated by a letter preceding this acronym (e.g. Af_{cb} for the A horizon developed under forest cover
136 in the Cambisol).

137 Selected soil samples have previously been analysed and described in detail (see Clymans et al. 2011,
138 Barão et al. 2014, Vandevenne and Barão et al. submitted). Basic soil property data including soil pH,
139 texture, soil organic carbon content, oxalate extracted Al and Fe for the selected samples are
140 reported in Table 1. Soil pH was determined in a CaCl₂ solution (0.01 M) and measured with a glass
141 electrode (Table 1) while soil organic carbon content was measured with Walkley and Black (1934)
142 titrations (Table 1). The grain size distribution reflects the difference in parent material between the
143 Luvisol and the Cambisol. The sandy Cambisols are more acidic and contain higher contents of SOC in
144 comparison to the Luvisols. The forested Cambisol has higher SOC contents and lower soil pH
145 compared to its arable counterpart. A comparable pattern is found for the Luvisol. In both cases SOC
146 decreases with depth, while soil pH increases.

147 Table 2 summarizes the results of the alkaline (Total AlkExSi, mg Si g⁻¹ – BSi & PSi), oxalate (Si_{oxalate})
148 results for the selected samples. The AlkExSi contents (mg Si g⁻¹) was quantified with the continuous
149 alkaline extraction (0.5 M NaOH) as described by Koning et al. (2002), to separate the extracted Si
150 into biogenic (BSi) and pedogenic Si (PSi, i.e. non-biogenic) (Table 2). The quantification of the
151 different AlkExSi fractions was based on the extracted Si/Al ratios as BSi was defined by a high Si/Al
152 ratio (>5). In both study areas, an evolution from BSi dominated (and virtual no PSi) to PSi dominated
153 (and virtually no BSi) horizons with depth was observed. Phytoliths were extracted from soils and
154 observed by microscopy in the O (for the forest soils) and A horizons, but were not observed deeper
155 in the soil profiles (Vandevenne and Barão et al. submitted), suggesting that only limited vertical
156 transport of phytoliths occurred at our sites (Fishkis et al. 2010a&b). The strong correlation between
157 the total PSi amount and Si_{oxalate} (Table 2) for the Cambisols indicates that the PSi mainly consists of Si
158 that is absorbed on Al and Fe-oxides (Barão et al. 2014). The pattern of Si and Al release observed
159 during the AlkExSi extraction for the Luvisol B-horizon samples was similar to that observed by
160 Koning et al. (2002) for illite and montmorillonite: this is to be expected given that these clay
161 minerals are dominant clay minerals in the Luvisol samples (Van Ranst et al 1982, Vandevenne and
162 Barão et al. submitted). The low amounts of Al and Fe extracted with oxalate from the Luvisol
163 samples suggest that the presence of Fe- and Al- oxides was limited (Table 1).

164 *2.2. Column experiment*

165 Soil columns were set up in duplicates for each of the eight soil horizons. 16 plastic columns of 10 cm
166 length and 6 cm internal diameter (i.e. two replicates for each combination of location, land use and
167 soil erosion) were filled up to 6 cm with air-dried soil sieved at two mm. Prior to the experiment the
168 columns were weighted to determine soil densities: densities varied significantly, between 1.08 and
169 1.77 kg m⁻³ (Table 1). The soil surface in the column was then covered with filter paper (Macherey-
170 Nagel MN640d 2.50 µm) to obtain a uniform wetting front. The columns were placed on porous
171 polyethylene plates covered by a Cole-Parmer Nylon–Polyamide-Membrane (pore size 0.45 µm),

172 covered with a cap to prevent evaporation and stored in the dark to prevent algae growth. Next,
173 columns were brought at field capacity by first saturating the porous plates at the bottom of the
174 column with water and consequently applying a negative pressure (-100 cm H₂O) with a vacuum
175 pump. A volume of 30 ml rain water was added to the columns to allow them to equilibrate during
176 two days. During the leaching test, the columns were irrigated with rain water collected during
177 August and September 2013 in Belgium (Heverlee) using a peristaltic pump. The rain water had a pH
178 of 7.2 and contained 1.27E-5 mol Si l⁻¹, 3.71E-8 mol Al l⁻¹, 8.34E-8 mol Ca l⁻¹, 1.72E-5 mol K l⁻¹, 1.58 E-5
179 mol Mg l⁻¹ and 3.85E-5 mol Na l⁻¹. In natural conditions, B horizons are percolated by ion rich soil
180 water coming from overlaying soil layers but using the same water for all columns allowed to
181 compare easily the effluents from the diverse columns. Initially we applied a flux of $0.8 \pm 0.2 \text{ cm d}^{-1}$
182 (Q_1), until DSi concentrations stabilized. After stabilization of the DSi concentration in the effluent,
183 we increased the water flux to $2 \pm 0.28 \text{ cm d}^{-1}$ (Q_2) in order to evaluate the effect of different
184 hydrological regimes on DSi release. The effluent was collected in plastic erlenmeyers (PP), sampled,
185 weighted and analysed for Si, Al, Ca, K, Mg and Na with ICP-OES (180 $\mu\text{L HNO}_3$) as well as for pH
186 measured with a glass electrode. At the start of the experiment, we sampled the effluent three times
187 a day. After three days sampling frequency was reduced to twice a day and after a week a daily
188 sampling frequency was used.

189 After the leaching experiment, we determined the pore volume (PV) and pore water velocity (v), for
190 both water fluxes. To estimate PV columns were irrigated with a pulse of 40 ml of 1 mM CaCl₂ after
191 the termination of the experiments. This allowed to avoid contamination with Ca²⁺ ions during the
192 leaching experiments. The breakthrough curve of Cl⁻ was then used to estimate the pore volume (PV)
193 and the pore water velocity (v) for each column using the advection-dispersion equation as
194 implemented in the CXTFIT2 model (Toride et al. 1995). Breakthrough curves did not show significant
195 asymmetry or tailing that would indicate the presence of physical non-equilibrium like preferential
196 flow paths or Cl⁻ adsorption on soil particles. For the initial flux (Q_1), we obtained estimates of v
197 between 1.3 and 2.3 cm d⁻¹ with an average of $1.8 \pm 0.34 \text{ cm d}^{-1}$, or $0.65 \pm 0.23 \text{ PV d}^{-1}$. Increasing the

198 flux 2.5 fold to $2 \pm 0.28 \text{ cm d}^{-1}$, gave v estimates between 2.7 and 4.8 cm d^{-1} with an average of 4.02
199 $\pm 0.61 \text{ cm d}^{-1}$ or $1.35 \pm 0.38 \text{ PV d}^{-1}$.

200 2.3. Si concentration

201 DSi concentrations ($[Si]_{aq}$, mg l^{-1}) were normalized (Si_{norm} , mg g^{-1}) for the water volume contained in
202 one pore volume of the considered column (V_{PV} , l) and in contact with amount of soil material
203 present (m_{soil} , g) (equation 1) to make results from different columns comparable. Thus, Si_{norm}
204 represents the mass (in mg Si) leaching out of one gram of soil.

$$205 \quad Si_{norm} = \frac{[Si]_{aq} V_{PV}}{m_{soil}} \quad \text{equation 1}$$

206 2.4. Si flux calculations

207 The Si flux was obtained by multiplying the average Si concentrations (C , mol DSi/l) by the water
208 discharge (Q_1 : $0.8 \pm 0.2 \text{ cm d}^{-1}$, Q_2 : $2 \pm 0.28 \text{ cm d}^{-1}$) and the cross-sectional area of the column (cm^2).

209 To quantify the effect of flux change on the quasi steady-state phase, we calculated the ratio
210 (equation 2) between the average Si flux (F_{min}), taken at Q_1 and Q_2 for each experiment. Only the last
211 five measurements taken at Q_1 were used as Si release at Q_1 typically declined semi-exponentially
212 throughout the experiment, reaching a steady value after a leaching period equal to one to three PV
213 (Fig.1, i.e. five last measurements). All observations were used at Q_2 as a steady dissolution rate was
214 obtained from on-set till end.

$$215 \quad \frac{F_{min2}}{F_{min1}} = \frac{C_2 Q_2 A}{C_1 Q_1 A} \quad \text{equation 2}$$

216 This allowed us to evaluate the influence of a water flux increase by a factor 2.5 on the Si flux.

217 2.5. Dissolution rates

218 Classically, dissolution rates are normalized against total reactive surface area measured with the BET
219 method (Brunauer et al. 1938) for a specific pure mineral. Unfortunately, for smectite holding soils

220 like ours (Vandevenne and Barão et al, submitted), the measurement of reactive surface area using
221 BET analysis does not estimate correctly the edge surface, where dissolution processes are dominant
222 (Zysset and Schindler 1996; Brantley and Mellott 2000).

223 Instead, we calculated the reactivity (r , mol kg⁻¹ s⁻¹) as the difference in Si concentration (mol l⁻¹)
224 between the influent ($[Si]_{in}$) and the effluent ($[Si]_{out}$) normalized against the mass of the sample (m ,
225 kg) (equation 3).

$$226 \quad r = \frac{q([Si]_{out} - [Si]_{in})}{m} \quad \text{equation 3}$$

227 The variation of dissolution rate over time was calculated for the low flux (Q_1 , q in m³ s⁻¹). The r -
228 values were used to identify the horizon with the most important Si release rates, including both
229 mineral weathering and dissolution of the AlkExSi phases. Typically, r -values declined more or less
230 exponentially with time which we attributed to the combined rapid release of AlkExSi and the slower
231 more constant release of Si through mineral dissolution. The period of AlkExSi release is therefore
232 defined by the inflection point of the curve (see detailed explanation discussion). To assess the
233 importance of the highly reactive Si fractions, we focused our analysis on the difference in reactivity
234 calculated from the first sample taken at the start of the experiment at flux Q_1 , which we compared
235 with that of the last sample taken at this flux.

236 *2.6. Controls on dissolution rates*

237 Reactivity may depend on soil pH, the presence of organic ligands, the CO₂ concentration, the
238 concentrations of Al and base cations as well as the amount of amorphous and crystalline Si present
239 in the soil. Therefore, dissolution rates can also be calculated as:

$$240 \quad r = k \frac{[H^+]}{[Al][BC]} \quad \text{equation 4}$$

241 The above equation is a simplification of the approach of Sverdrup and Warfvinge (1988), which also
242 takes into account CO₂ pressure and organic ligands which were not measured in our experiments. As

243 pH is altered by the presence of the organic acids and eventual variations in CO₂ partial pressure, pH
244 will accommodate to some extent the effects these controls may have (Hinsinger et al., 2001). The
245 constant k was a dissolution constant of all soil particles.

$$246 \quad k = \alpha k_{MSi} + \beta k_{AlkExSi} \quad \text{equation 5}$$

247 k_{MSi} and $k_{AlkExSi}$ are the dissolution constants for respectively silicate minerals and AlkExSi (i.e. PSi and
248 BSi), while α and β are their respective proportions. The k_{MSi} is determined by the bulk mineralogy of
249 the parent material, which is different for the Luvisol and Cambisol. In order to assess the individual
250 effects of pH and BC concentrations on solubility we transformed eq. 4 as follows:

$$251 \quad r \frac{[Al]}{[H^+]} = k_1 \quad \text{equation 6}$$

$$252 \quad r[BC] = k_2 \quad \text{equation 7}$$

$$253 \quad r \frac{[Al][BC]}{[H^+]} = k_1 \quad \text{equation 8}$$

254 k_1 represents the reactivity of soils A and B neglecting the influence of pH and Al while in the
255 calculation of k_2 the effect of base cations (BC, grouping K⁺, Na⁺, Ca²⁺, Mg²⁺) is neglected. In eq. 8 all
256 controlling effects are combined.

257 The resulting values can be easily interpreted. If a difference in original Si release rates ($r_1 \neq r_{1i}$)
258 disappears after the elimination of a parameter ($k_{1i} \approx k_{1i}$), this suggests that this parameter controls
259 the observed differences in release rates. As we investigated land use and soil horizon effects we
260 investigated whether differences in Si release (r) between two land uses and horizons were still
261 apparent if the effect of a given parameter was eliminated.

262

263 **3. Results**

264 *3.1. Si release from A and B horizons*

265 Table 3 gives all element concentrations in ppm and pH measured in all leachates. Leached
266 normalized Si concentrations (Si_{norm}) at flux Q_1 were plotted against cumulative PV leached through
267 the columns to allow comparison between the different soils (Figure 1). No significant differences in
268 absolute values were observed between the replicate columns. We identified two types of response.
269 The first type of response consisted of high DSi concentrations at the start followed by a rapid
270 decrease until an inflection point was reached, whereafter the further decline of the DSi
271 concentration was very slow and occurred at a constant rate. In the second type of response, DSi
272 concentrations were relatively low at the beginning of the experiment and decreased continuously at
273 a low rate from the beginning to the end of the experiment. This second type of curve was not
274 observed for the elements Ca, Na and Mg.

275 All A horizon samples with the exception of the arable land on Luvisol showed a response of the first
276 type. The inflection point for the Cambisol soils equaled about 1 PV_{cum} , while the inflection point for
277 the forested Luvisol site equaled 1.5 PV_{cum} . All B horizon samples, on the other showed a response of
278 the second type.

279 For a given site and land use type, the amount of Si released (Figure 1) from the A horizons (0.5-36.2
280 $\mu\text{g.g}^{-1}$) always significantly exceeded Si loss from B horizons (0.6-3.5 $\mu\text{g.g}^{-1}$) ($t(141) = 9.49, p < 0.05$). If
281 we compared land use types, forest sites released significantly more Si (1.9 – 18.8 $\mu\text{g.g}^{-1}$ in Luvisol,
282 5.0 – 36.2 $\mu\text{g.g}^{-1}$ in Cambisol) than arable land (0.5-1.5 $\mu\text{g.g}^{-1}$ in Luvisol, 1.3 – 9.6 $\mu\text{g.g}^{-1}$ in Cambisol)
283 ($t(146) = 23.59, p < 0.05$). In other words, *Af* released the highest Si_{norm} .

284 The initial DSi release initially correlated well with the BSi amounts present in the soil. No correlation
285 between P*Si* amounts and initially or finally released DSi were observed (Figure 2). The lower Si
286 release from *Ac* compared to *Af* may therefore be attributed to the lower amounts of BSi present in
287 the samples (Table 2). Differences in BSi storage also explain why an exponential decline was clearly
288 observed for *Ac_v* samples and not for *Ac_{cb}* samples. Besides the lower BSi content of the *Ac_{cb}* samples,
289 the low initial concentrations observed for these samples may also be explained by the fact that it is

290 likely that, over a period of centuries, the most soluble BSi fraction has been removed without
291 replenishment from these intensively cultivated soils. As agriculture in Sweden is less intensive with
292 frequent ley periods, the BSi pool is periodically partially replenished with highly reactive BSi, which
293 responds rapidly to leaching (Figure 2).

294 The presence of a larger BSi pool cannot be the only factor explaining the higher Si release under
295 forest. The differences in Si release were much larger (by a factor 3 for the Cambisol and a factor 10
296 for the Luvisol) than the differences in BSi pools present in the A horizon samples (factor 2). Although
297 patterns in Si release were generally identical for the same land use, the Cambisol soils produced
298 significantly higher Si concentrations than the Luvisol soils ($t(145)=19.65, p<0.05$). These soils were
299 also more acid. In general, the Si normalized concentration (Si_{norm}) decreased with increasing pH in
300 the effluents (Figure 3). Si release was drastically higher at pH lower than 4 (Figure 3).

301 *3.2. Equilibrium dissolution flux*

302 Under forest, the DSi concentrations were statistically significantly lower when the flux was doubled,
303 except for the Bf_{iv} horizon (Figure 4). Consequently the Si flux ratios (Table 4, equation 2) in forests
304 were lower (1.36-2.10) than 2.5 (factor of water flux increase), especially for the Af horizon (1.36). In
305 contrast, DSi concentrations did not show a significant decrease for the cropland sites and flux ratios
306 were closer to 2.5, especially in c_{cb} samples where DSi concentrations appeared to be near-
307 independent of the water flux and ratios equal the increase factor of water flux.

308 Thus, Si export is in equilibrium for Luvisol cropland samples but is clearly transport controlled in the
309 acidic Cambisol forest samples. For other samples, the situation is intermediate. At present, we do
310 not fully understand the reasons for this variation. The difference in response to a flux increase of the
311 different DSi sources may explain the different behavior. Indeed, the observed flux ratio is generally
312 high for samples with a low BSi content. This suggests that solution of mineral Si is in equilibrium,
313 while the dissolution of BSi is, at least partly transport-controlled (Figure 5). Alternatively, the effect

314 of pH may be important, whereby Si solution is in equilibrium at high pH (arable sites) values and this
315 equilibrium is not achieved at lower pH values (forested sites) (Figure 5).

316 3.3. Si dissolution rates

317 Figure 6 shows the logarithmic values of dissolution rates (r in $\text{mol g}^{-1}\text{s}^{-1}$, equation 3), the k_1 -values
318 (equation 6), the k_2 -values (equation 7) and the apparent dissolution constant (k , equation 8)
319 calculated for the beginning (i) and the end of the leaching tests (f).

320 The dissolution rates r were higher under forest cover than under arable land. The k_1 -values, the
321 dissolution rates independent of pH, were higher for the A (dots in Figure 6) than for B horizons for
322 all sites (triangles in Figure 6). The highest k_1 -values were recorded for the Af horizon while the Bf
323 horizon had the lowest values. During the experiment the k_1 -value decreased, except for Ac_{IV} .

324 Considering only the effect of base cations (k_2), the calculated constants were several orders of
325 magnitude lower than the dissolution rate. k_2 -values were higher for forests than for croplands (i.e.
326 they were also dependent on land use) as it was the case for the dissolution rates (r). The k_2 -values
327 also declined during the experiment (Figure 6).

328 The k -values, which should approximate the true dissolution constant after correction for pH and BC,
329 were of the same order of magnitude than k_2 -values. However, as is the case for k_1 , the land use
330 differentiation noticed for r -values disappeared and A horizons showed higher apparent dissolution
331 constants (k) than B horizons. The differentiation between both horizons was more pronounced (ca
332 1-2 orders of magnitude) for k -values in comparison to k_2 -values. k -values also declined with time for
333 all samples. For the A horizon the values decreased 2 orders of magnitude except for c_{cb} for which
334 the decrease was less important.

335 4. Discussion

336 Our experiments not only allowed to quantify DSi mobility but also to investigate the effect of water
337 chemistry and transport parameter on DSi fluxes. The experimental data did show important

338 differences in DSi release rates between sites, soil horizons and over time. DSi release from Af
339 samples was strongly time dependent and decreased rapidly with time. This was not the case for Bf
340 samples nor for arable land soils, with the exception of the Ac_{cb} horizon. Our key observations can be
341 summarized as follows:

- 342 - DSi dissolution rates (r) were generally higher for A horizons in comparison to B horizons and
343 for forest soils in comparison to arable land soils.
- 344 - Doubling the water flux affected DSi concentrations differently for forest soils in comparison
345 to arable land soils.
- 346 - More DSi was released from the Cambisol soils in comparison to the Luvisol soils.

347 Here, we propose a conceptual model explaining our key observations as summarized above.

348 *4.1. Time dependency of DSi concentrations*

349 A rapid exponential decrease in DSi concentrations over time (Figure 1) was observed for all samples
350 containing high BSi amounts ($>3 \text{ mg.g}^{-1}$), i.e. all **A horizons** except Ac_{lv} . The rapid decrease can be due
351 to dissolution of fine grained particles and/or very reactive particles or desorption processes (Evans
352 and Banwart 2006) which both can be described by parabolic kinetics (Brantley et al. 2008). Si
353 desorption processes are less likely to occur. Si should desorb from Fe and Al-(hydr)oxides
354 (McKeague and Cline 1963), which contents are low in the A horizons, except in f_{cb} (Table 1;
355 Vandevenne and Barão et al. submitted, Barao et al. 2014). The low Si concentrations measured by
356 oxalate extraction ($<0.25 \text{ mg g}^{-1}$ in the Luvisol (Vandevenne and Barão, submitted) and $< 0.40 \text{ mg g}^{-1}$
357 in the A horizons of the Cambisol (Table 2, Barão et al. 2014)) confirm that Si desorption is a minor
358 source of Si release. The decrease in k-values observed between the start and the end of the
359 experiment suggests that the dominant source of Si shifted from a highly reactive source at the start
360 of the experiment to a less reactive source during the leaching test. The highly reactive source is
361 most likely the BSi present in both A horizons of the Luvisols and Cambisols. Curves are similar to the
362 curves obtained in phytolith (BSi) dissolution experiments (Frayse et al. 2009). At the start of the

363 experiment, maximum Si concentrations measured in the *A_f* columns approached equilibrium
364 concentrations of phytolith dissolution (60 - 100 mg/l; Fraysse et al. 2009). Mass-normalized
365 dissolution rates of phytoliths are similar for different plant species (Fraysse et al. 2009). Hence, the
366 much lower initial Si release for arable topsoil compared to forest topsoil can be partly attributed to
367 the fact that forests store up to double amounts of BSi (Figure 2, Clymans et al. 2011). The high Si
368 release from *A_f* soils is also in agreement with results from other studies in temperate forests where
369 Si concentrations measured in soil pore water could not be explained by mineral weathering only
370 (Farmer 2005; Gérard et al. 2008; Sommer et al. 2013). BSi dissolution can also explain the high Si
371 release from the *A_{c_{cb}}* samples. However, the *A_{c_{lv}}* samples also contain significant amounts of BSi but
372 do not show a rapid initial release of BSi. This shows that not only the type of Si is controlling its
373 solubility: phytoliths in the *A_{c_{lv}}* horizon may be less soluble because they form a residual, less soluble
374 residual and/or by secondary change such as the deposition of an oxide coating on their surface
375 (Piperno 2006).

376 CaCl₂ extractions on the forest soils (Table 2) and on Cambisol, Podzol and Luvisol (Georgiadis et al.
377 2013) revealed higher Si concentrations from the B horizon compared to the A horizon. However Si
378 release curves for the B horizons did not show high concentrations or a rapid initial decline like the A-
379 horizon suggesting the absence of a highly reactive fraction. Initial and final Si_{norm} of our experiment
380 did not correlate with P_{Si} concentrations in the soil samples, determined with alkaline extraction
381 methods (Figure 2). A rapid release of Si from P_{Si} in the B horizon was not observed in the conditions
382 of this experiment. The slow decline in Si concentrations measured in the final stage of the
383 experiments was similar for A horizon and B horizon samples.

384 The low *k*-values and small difference in *k*-values over time for each B horizon equally suggest that Si
385 released in B horizons are controlled by slow dissolution processes near equilibrium, i.e. mineral
386 dissolution. The final dissolution rates that we observe are indeed similar to those observed in
387 mineral dissolution experiments and field measurements (Figure 7) (Köhler et al. 2003; Golubev et al.

388 2005; Köhler et al. 2005; Godd ris et al. 2006; Golubev et al. 2006; Frayse et al. 2009). Given the fact
389 that observed k -values are similar, it is reasonable to assume that mineral dissolution is also the main
390 contributor to Si release towards the end of the experiments for A_{cb} horizon samples and during the
391 whole experiment for the A_{Civ} horizon samples.

392 We found that Si concentrations in soil pore water from A horizons are controlled by BSi dissolution
393 combined with mineral dissolution, confirming a suggestion by Farmer et al. (2005). Correspondingly
394 initial r -values were higher than final r -values but they still plotted in the range of mineral dissolution
395 rates and did not reach phytolith dissolution rates, which are 100 to 10000 times higher (Figure 7).
396 Since phytolith and mineral dissolution rates in Figure 7 are normalized to reactive surface area
397 (unlike our r -values), uncertainties with regard to the surface specific areas could exaggerate the
398 difference between phytoliths and rock-forming minerals. Even more importantly the analysed
399 natural soils consist of a mixture of minerals and relatively low amounts of BSi (<10 mg.g⁻¹): overall
400 dissolution rates are therefore expected to be much lower than those measured for pure phytolith.
401 Assuming a phytolith concentration of 10 mg g⁻¹, one would expect the overall dissolution rate to
402 double, for phytoliths which would be 100 times more soluble than mineral Si.

403 *4.2. Differences in DSi dissolution rates*

404 The higher BSi storage in the A horizon of forest alone is insufficient to explain the discrepancy in Si
405 release from A horizons between forests and low-intensity agricultural sites. Differences in Si release
406 were higher than differences in BSi pools under cropland in comparison to A horizons under forest.
407 All r -values were higher in soils characterized by low pH values and high soil organic carbon contents
408 (Table 1). We observed strongly increased normalized Si concentrations at pH<4, acid conditions
409 typical for A-horizons under forest (Figure 3, Table 1). Furthermore, when soil acidity was corrected
410 for by calculating k_1 , land use effects were no longer present (Figure 6). Both observations suggest
411 that dissolution rates of both BSi (r_i) and minerals (r_f) were dependent on soil pH resulting in a
412 decline of Si release along the land use gradient, from forest to intensively used cropland (Figure 2).

413 Other studies already showed enhanced mineral weathering and Si release in environments at pH 4-
414 5, and enhanced weathering in presence of vegetation (Drever 1994; Cochran and Berner 1996). This
415 may also explain why concentrations of Ca, Mg and Na were at least two times higher in the A
416 horizons compared to the B horizon of the same soil (Table 3).

417 The production of H⁺ protons, CO₂ and organic acids related to organic matter in the rhizosphere not
418 only affect the pH of the soil but also produces root exudates which enhances weathering by ligand
419 exchange and complexation processes (Drever and Stillings 1997; Kelly et al. 1998; Hinsinger et al.
420 2006). The strong correlation between organic matter content and pH made it impossible to identify
421 the effects that these other factors may have separately on Si solubility. Similarly, silicate weathering
422 may be enhanced by the production of nitric acid after N fertilizer application (Pacheco et al. 2013).
423 A follow-up study that focuses on separating the effects of these different dissolving agents (e.g.
424 organic ligands, nitrates,...) is necessary to identify how they affect Si release.

425 *4.3. Turnover rates*

426 The contribution of the easily soluble Si phase, consisting dominantly of BSi (see section 4.1), and less
427 soluble Si phase, i.e. mineral Si (MSi), were separated to determine the BSi turnover rates in the A
428 horizon. The MSi contributions were assumed to correspond with the final stable part of the
429 dissolution curve. Because we could not distinguish a specific PSi signal in the B-horizon, where this
430 fraction is the dominant AlkExSi fraction (Table 2), we included its contribution in our MSi estimate.
431 Afterwards, we linearly extrapolated the concentrations from the stable part of the A horizon to the
432 start of the experiment (Figure 8, 9). The corresponding Si amount was subtracted from the total
433 amount of Si released to obtain the amount Si coming from BSi (grey zone in Figures 8, 9). Assuming
434 a constant water flux of 0.8 cm/d, turnover rates (*T*) could then be calculated as follows:

$$435 \quad T = \frac{[BSi] * m_{col}}{\frac{\int_V^0 c_{tot}(V) \delta V - \int_V^0 c_{min}(V) \delta V}{t}} \quad \text{equation 9}$$

436 Where $[BSi]$ was the concentration of BSi in soil (mg g^{-1}), m_{col} was the mass of dried soil in the column
437 (g), $C(V)$ the concentration in function of the volume for the total curve and the mineral contribution
438 and t is the time in days. For f_{lv} the turnover rates were on average 11 ± 4.2 yr, while for the f_{cb}
439 turnover rates were 13.3 ± 12.2 yr. For c_{cb} , turnover rates were 38.1 ± 6.8 yr, suggesting that the BSi
440 present in these samples was less soluble in comparison to the BSi present in the forest soils (Figure
441 9). No BSi release could be detected for the c_{lv} samples, despite the presence of significant BSi
442 amounts, suggesting an even longer turnover rate.

443 Turnover times of phytoliths extracted from plants were estimated to vary from 0.5 to 2.4 yr in
444 plants ((Bartoli and Souchier 1978) and from 0.5 to 3 yr in soil solutions at pH 4 to 5 (Frayse et al.
445 2009). Turnover times would vary from 6 to 18 months for phytoliths in the litter of tropical forests
446 (Alexandre et al. 1994) from 2 to 10 yr in litter and from 1 to 300 yr in Podzol (Bartoli and Souchier
447 1978). Longer turnover times were estimated for phytoliths in grassland soils: from 250 yr to 1300 yr
448 (Blecker et al. 2006). Our estimations fit in the range calculated by Bartoli and Souchier (1978) for
449 soils but our values were calculated from column experiments where dissolution processes are likely
450 to be accelerated compared to field situations (White and Brantley 2003). The difference in turnover
451 rates between the Cambisol cropland and forest samples indicates that the BSi present in c_{cb} may
452 indeed partly be the product of the selective dissolution of the most soluble BSi fraction under arable
453 land use. This process may have progressed further on the intensively farmed Luvisol cropland, so
454 that only a relatively insoluble BSi fraction remains.

455 5. Conclusion

456 Our column experiments did allow to gain insight in the mechanisms controlling Si release from soils
457 under different land use in Sweden and Belgium. As proposed by Farmer (2005), the amount of BSi
458 present in the soils is an important control on DSi release. However, our experiments show that the
459 presence of BSi is not the only factor controlling Si release: hydrological conditions and soil acidity

460 strongly affects dissolution of both BSi and MSi. Additional knowledge on the type of
461 acidifying/dissolving agents is required to disentangle their exact effect.

462 The fact that pH has an important effect on BSi release implies that the release of BSi after
463 deforestation will not only depend on the rate at which the BSi reservoir is depleted, but also on the
464 evolution of the pH of the soil's A-horizon. The latter will be affected not only by natural conditions
465 (e.g. acidic vs. basic bedrock) but also by human action: in Belgium, farmers are known to have
466 increased the pH of agricultural land by liming for many centuries, if not millennia (Vanwalleghem et
467 al. 2004) but this may not have occurred everywhere as this requires an accessible source of CaCO_3 is
468 required.

469 While our experiments allowed identifying factors controlling Si mobility, they also entail limitations
470 and do not allow to fully describe DSi dynamics in the soils that we studied. The sources and sinks of
471 DSi in soils can differ depending on the pedological conditions (Cornelis et al. 2014). Under natural
472 conditions rain water would have leached the A horizon before it reaches the B horizon. The pore
473 water reaching the B horizon is therefore likely to contain significant amounts of DSi which may
474 precipitate in the B horizon where conditions are less acidic (Kendrick and Graham 2004; Saccone et
475 al. 2008). The amount of Si exported from the B horizon would in that case be controlled by
476 saturation indexes of secondary minerals and/or the Si sorption capacity of the soil. Furthermore,
477 the final amount of Si released by the soil system will strongly depend on the hydrological
478 functioning of the landscape. A land use change from forest to arable land strongly affects
479 hydrological pathways and will therefore have important implications for the residence time of water
480 as the rate of flow through the different water reservoirs present in the landscape.

481 A full comprehension of the effects of land use change on Si release therefore not only requires
482 further research on the solubility of different Si fractions present in soils under natural conditions
483 (Sauer et al 2006, Georgiadis et al 2013, Barão et al 2014) but also the development and
484 operationalization of coupled geochemical-hydrological models that would allow to assess the

485 combined effect of geochemical (amounts of BSi, pH, ...) and hydrological (water fluxes) changes
486 (Maher 2010) .

487

488

489 **Acknowledgements**

490 The authors thank Länsstyrelsen in Kronobergslän for consenting to fieldwork in the nature reserve
491 Siggaboda and culture reserve Råshult, Agentschap voor Natuur and Bos for consenting to fieldwork
492 in Meerdaal forest. The following persons are thanked for their invaluable assistance: L. Fondu, V.
493 Tuts, E. Vassilieva, F. Schoovaerts (KU Leuven) for helping to set up and follow up the experiment. B.
494 Ronchi would like to thank the Flemish Agency for the promotion of Innovation by Science and
495 Technology (IWT) for providing a PhD grant. E. Struyf acknowledges the Research Foundation
496 Flanders (FWO) for funding his postdoctoral position. F. Vandevenne and A. L. P. Barão would like to
497 thank BOF-UA for PhD fellowship funding. We would like to thank BELSPO for funding project SOGLO
498 and FWO for funding of project G043313N. Prof. Jan Diels is thanked for his critical remarks on an
499 earlier version of this manuscript.

500 **References**

- 501 Alexandre A, Colin F, Meunier J (1994) Phytoliths as indicators of the biogeochemical turnover of
502 silicon in equatorial rainforest. *CR Acad Sci Paris* 319:453–458.
- 503 Barão AL, Clymans W, Vandevenne F, et al. (2014) Pedogenic and biogenic alkaline extracted Si
504 distributions along a temperate land use gradient. *Eur. J. Soil Sci.*
- 505 Bartoli F, Souchier B (1978) Cycle et rôle du silicium d'origine végétale dans les écosystèmes
506 forestiers tempérés. *Ann Sci For* 35:187–202.
- 507 Bartoli LP, Wilding F (1980) Dissolution of biogenic opal as a function of its physical and chemical
508 properties. *Soil Sci Soc Am J* 44:873–878.
- 509 Bartoli F (1985) Crystallochemistry and surface properties of biogenic opal. *J Soil Sci* 36:335–350. doi:
510 10.1111/j.1365-2389.1985.tb00340.x

- 511 Beckwith RS, Reeve R (1963) Studies on soluble silica in soils I. The sorption of silicic acid by soils and
512 minerals. *Aust J Soil Res* 1:157–68.
- 513 Blecker SW, McCulley RL, Chadwick O a., Kelly EF (2006) Biologic cycling of silica across a grassland
514 bioclimate sequence. *Global Biogeochem Cycles* 20:1–11. doi: 10.1029/2006GB002690
- 515 Brantley SL, Mellott NP (2000) Surface area and porosity of primary silicate minerals. *Am Mineral*
516 85:1767–1783.
- 517 Brantley SL, Kubicki J, White A (2008) Kinetics of Mineral Dissolution. In: Brantley SL, Kubicki JD,
518 White AF (eds) *Kinet. Water-Rock Interact.* pp 151–210
- 519 Brunauer S, Emmett PH, Teller E (1938) Adsorption of Gases in Multimolecular Layers. *J Am Chem Soc*
520 60:309–319.
- 521 Cama J, Ganor J (2006) The effects of organic acids on the dissolution of silicate minerals: A case
522 study of oxalate catalysis of kaolinite dissolution. *Geochim Cosmochim Acta* 70:2191–2209. doi:
523 10.1016/j.gca.2006.01.028
- 524 Cardinal D, Gaillardet J, Hughes HJ, et al. (2010) Contrasting silicon isotope signatures in rivers from
525 the Congo Basin and the specific behaviour of organic-rich waters. *Geophys Res Lett* 37:n/a–
526 n/a. doi: 10.1029/2010GL043413
- 527 Carey JC, Fulweiler RW (2011) Human activities directly alter watershed dissolved silica fluxes.
528 *Biogeochemistry*. doi: 10.1007/s10533-011-9671-2
- 529 Chadwick OA, Hendricks DM, Nettleton WD (1987) Silica in Duric Soils: I. A Depositional Model. *Soil*
530 *Sci. Plant Nutr.* 51: 975-982
- 531 Clymans W, Struyf E, Govers G, et al. (2011) Anthropogenic impact on biogenic Si pools in temperate
532 soils. *Biogeosciences* 8: 2281-2293.
- 533 Cochran MF, Berner R a. (1996) Promotion of chemical weathering by higher plants: field
534 observations on Hawaiian basalts. *Chem Geol* 132:71–77. doi: 10.1016/S0009-2541(96)00042-3
- 535 Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. *Global*
536 *Biogeochem Cycles* 16:1–8. doi: 10.1029/2002GB001894
- 537 Conley DJ, Likens GE, Buso DC, et al. (2008) Deforestation causes increased dissolved silicate losses in
538 the Hubbard Brook Experimental Forest. *Glob Chang Biol* 1–7. doi: 10.1111/j.1365-
539 2486.2008.01667.x
- 540 Cornelis J-T, Delvaux B, Cardinal D, et al. (2010) Tracing mechanisms controlling the release of
541 dissolved silicon in forest soil solutions using Si isotopes and Ge/Si ratios. *Geochim Cosmochim*
542 *Acta* 74:3913–3924. doi: 10.1016/j.gca.2010.04.056
- 543 Cornelis J-T, Dumon M, Tolossa AR, et al. (2014) The effect of pedological conditions on the sources
544 and sinks of silicon in the Vertic Planosols in south-western Ethiopia. *Catena* 112:131–138. doi:
545 10.1016/j.catena.2013.02.014

- 546 DeMaster DJ (1981) The supply and accumulation of silica in the marine environment. *Geochim*
547 *Cosmochim Acta* 45:1715–1732. doi: 10.1016/0016-7037(81)90006-5
- 548 Derry L a, Kurtz AC, Ziegler K, Chadwick O a (2005) Biological control of terrestrial silica cycling and
549 export fluxes to watersheds. *Nature* 433:728–31. doi: 10.1038/nature03299
- 550 Dixon J B, Weed SB (1989) Minerals in soil environments, 2nd ed., Minerals in soil environments, Soil
551 Sci Soc Am J, Madison, Wisconsin, USA
- 552 Doucet FJ, Schneider C, Bones SJ, et al. (2001) The formation of hydroxyaluminosilicates of
553 geochemical and biological significance. *Geochim Cosmochim Acta* 65:2461–2467.
- 554 Dove PM (1995) Kinetic and thermodynamic controls on silica reactivity in weathering environments.
555 In: White A, Brantley S (eds) *Chem. Weather. rates Silic. Miner., Mineralogi.* Washington D.C.,
556 pp 235–290
- 557 Dove PM, Han N, Wallace AF, De Yoreo JJ (2008) Kinetics of amorphous silica dissolution and the
558 paradox of the silica polymorphs. *Proc Natl Acad Sci U S A* 105:9903–8. doi:
559 10.1073/pnas.0803798105
- 560 Drever JI (1994) The effect of land plants on weathering rates of silicate minerals. *Geochim*
561 *Cosmochim Acta* 58:2325–2332. doi: 10.1016/0016-7037(94)90013-2
- 562 Drever JI, Stillings LL (1997) The role of organic acids in mineral weathering. *Colloids Surfaces A*
563 *Physicochem Eng Asp* 120:167–181. doi: 10.1016/S0927-7757(96)03720-X
- 564 Evans KA, Banwart SA (2006) Rate controls on the chemical weathering of natural polymineralic
565 material . I . Dissolution behaviour of polymineralic assemblages determined using batch and
566 unsaturated column experiments. *Appl Geochemistry* 21:352–376. doi:
567 10.1016/j.apgeochem.2005.10.001
- 568 Farmer VC (2005) Forest vegetation does recycle substantial amounts of silicon from and back to the
569 soil solution with phytoliths as an intermediate phase, contrary to recent reports. *Eur J Soil Sci*
570 56:271–272. doi: 10.1111/j.1365-2389.2005.00695.x
- 571 Fishkis O, Ingwersen J, Lamers M, et al. (2010a) Phytolith transport in soil: a laboratory study on
572 intact soil cores. *Eur J Soil Sci* 61:445–455. doi: 10.1111/j.1365-2389.2010.01257.x
- 573 Fishkis O, Ingwersen J, Lamers M, et al. (2010b) Phytolith transport in soil: A field study using
574 fluorescent labelling. *Geoderma* 157:27–36. doi: 10.1016/j.geoderma.2010.03.012
- 575 Fraysse F, Pokrovsky OS, Schott J, Meunier J-D (2006) Surface properties, solubility and dissolution
576 kinetics of bamboo phytoliths. *Geochim Cosmochim Acta* 70:1939–1951. doi:
577 10.1016/j.gca.2005.12.025
- 578 Fraysse F, Pokrovsky OS, Schott J, Meunier J-D (2009) Surface chemistry and reactivity of plant
579 phytoliths in aqueous solutions. *Chem Geol* 258:197–206. doi: 10.1016/j.chemgeo.2008.10.003
- 580 Frings PJ, Clymans W, Jeppesen E, et al. (2014) Lack of steady-state in the global biogeochemical Si
581 cycle: emerging evidence from lake Si sequestration. *Biogeochemistry*. doi: 10.1007/s10533-
582 013-9944-z

- 583 Garrels RM, Mackenzie FT (1967) Origin of the Chemical Compositions of Some Springs and Lakes. In:
584 Stumm W (ed) *Equilib. Concepts Nat. Water Syst. Adv. Chem. Ser. No. 67*. American Chemical
585 Society, Washington, pp 222–242
- 586 Georgiadis A, Sauer D, Herrmann L, et al. (2013) Development of a method for sequential Si
587 extraction from soils. *Geoderma* 209-210:251–261. doi: 10.1016/j.geoderma.2013.06.023
- 588 Gérard F, Mayer KU, Hodson MJ, Ranger J (2008) Modelling the biogeochemical cycle of silicon in
589 soils: Application to a temperate forest ecosystem. *Geochim Cosmochim Acta* 72:741–758. doi:
590 10.1016/j.gca.2007.11.010
- 591 Goddérés Y, François LM, Probst A, et al. (2006) Modelling weathering processes at the catchment
592 scale: The WITCH numerical model. *Geochim Cosmochim Acta* 70:1128–1147. doi:
593 10.1016/j.gca.2005.11.018
- 594 Golubev SV, Pokrovsky OS, Schott J (2005) Effect of dissolved CO₂ on the dissolution kinetics of basic
595 silicates at 25 °C. *Chem Geol* 217:227–238.
- 596 Golubev S V., Bauer A, Pokrovsky OS (2006) Effect of pH and organic ligands on the kinetics of
597 smectite dissolution at 25°C. *Geochim Cosmochim Acta* 70:4436–4451. doi:
598 10.1016/j.gca.2006.06.1557
- 599 Guntzer F, Keller C, Meunier JD (2011) Benefits of plant silicon for crops: a review. *Agron. Sustain. Dev.*
600 32: 201-213.
- 601 Hinsinger P, Fernandes Barros ON, Benedetti MF, et al. (2001) Plant-induced weathering of a basaltic
602 rock: experimental evidence. *Geochim Cosmochim Acta* 65:137–152. doi: 10.1016/S0016-
603 7037(00)00524-X
- 604 Hinsinger P, Plassard C, Jaillard B (2006) Rhizosphere: A new frontier for soil biogeochemistry. *J*
605 *Geochemical Explor* 88:210–213. doi: 10.1016/j.gexplo.2005.08.041
- 606 Jackson RB, Schenk H., Jobbagy EG, et al. (2000) Belowground consequences of vegetation change
607 and their treatment in models. *Ecol Appl* 10:470–483.
- 608 Keller C, Guntzer F, Barboni D, Labreuche J, et al (2012) Impact of agriculture on the Si biogeochemical
609 cycle: Input from phytolith studies. *Comptes Rendus geosci.* 344: 739-746.
- 610 Kelly EF, Chadwick OA, Hilinski TE (1998) The effect of plants on weathering. *Biogeochemistry* 42:21–
611 53.
- 612 Kendrick KJ, Graham RC (2004) Pedogenic Silica Accumulation in Chronosequence Soils, Southern
613 California. *Soil Sci Soc Am J* 68:1295–1303.
- 614 Köhler S, Dufaud F, Oelkers EH (2003) An experimental study of illite dissolution kinetics as a function
615 of pH from 1.4 to 12.4 and temperature from 5 to 50 °C. *Geochim Cosmochim Acta* 67:3583–
616 3594.
- 617 Köhler SJ, Bosbach D, Oelkers EH (2005) Do clay mineral dissolution rates reach steady state?
618 *Geochim Cosmochim Acta* 69:1997–2006. doi: 10.1016/j.gca.2004.10.015

- 619 Koning E, Epping E, Raaphorst WIMVAN (2002) Determining Biogenic Silica in Marine Samples by
620 Tracking Silicate and Aluminium Concentrations in Alkaline Leaching Solutions. *Aquat*
621 *Geochemistry* 8:37–67.
- 622 Laruelle GG, Roubeyx V, Sferratore a., et al. (2009) Anthropogenic perturbations of the silicon cycle at
623 the global scale: Key role of the land-ocean transition. *Global Biogeochem Cycles* 23:1–17. doi:
624 10.1029/2008GB003267
- 625 Lucas Y (2001) The role of plants in controlling rates and products of weathering: Importance of
626 Biological Pumping. *Annu Rev Earth Planet Sci* 29:135–63.
- 627 Maher K (2010) The dependence of chemical weathering rates on fluid residence time. *Earth Planet*
628 *Sci Lett* 294:101–110. doi: 10.1016/j.epsl.2010.03.010
- 629 McKeague JA, Cline MG (1963) Silica in soil solutions II. 'The adsorption of monosilicic acid by soil and
630 by other substances'. *Can J Soil Sci* 43:83–96.
- 631 Moulton KL, West J, Berner RA (2000) Solute flux and mineral mass balance approaches tot the
632 quantification of plant effects on silicate weathering. *Am J Sci* 300:539–570.
- 633 Neal C (1996) Towards lumped integrated models of complex heterogeneous environmental systems.
634 *Sci Total Environ* 183:115–124. doi: 10.1016/0048-9697(95)04976-2
- 635 Neal C (1997) A view of water quality from the Plynlimon watershed. *Hydrol Earth Syst Sci* 1:743–753.
636 doi: 10.5194/hess-1-743-1997
- 637 Oliva P, Viers J, Dupré B (2003) Chemical weathering in granitic environments. *Chem Geol* 202:225–
638 256. doi: 10.1016/j.chemgeo.2002.08.001
- 639 Pacheco FAL, Landim PMB, Szocs T (2013) Anthropogenic impacts on mineral weathering: A statistical
640 perspective. *Appl Geochemistry* 36:34–48. doi: 10.1016/j.apgeochem.2013.06.012
- 641 Piperno DR (2006) *Phytoliths. A comprehensive guide for archeologists and paleoecologists.* AltaMira
642 Press (Rowman & Littlefield), Lanham, New York, Toronto, Oxford.
- 643 Saccone L, Conley DJ, Likens GE, et al. (2008) Factors that Control the Range and Variability of
644 Amorphous Silica in Soils in the Hubbard Brook Experimental Forest. *Soil Sci Soc Am J* 72:1637.
645 doi: 10.2136/sssaj2007.0117
- 646 Sauer D, Saccone L, Conley DJ, et al. (2006) Review of methodologies for extracting plant-available
647 and amorphous Si from soils and aquatic sediments. *Biogeochemistry* 80:89–108. doi:
648 10.1007/s10533-005-5879-3
- 649 Sommer M, Kaczorek D, Kuzyakov Y, Breuer J (2006) Silicon pools and fluxes in soils and landscapes—
650 a review. *J Plant Nutr Soil Sci* 169:310–329. doi: 10.1002/jpln.200521981
- 651 Sommer M, Jochheim H, Höhn a., et al. (2013) Si cycling in a forest biogeosystem – the importance of
652 transient state biogenic Si pools. *Biogeosciences* 10:4991–5007. doi: 10.5194/bg-10-4991-2013

653 Street-perrott FA, Barker PA (2008) Biogenic silica : a neglected component of the coupled global
654 continental biogeochemical cycles of carbon and silicon. *Earth Surf Process Landforms* 33:1436–
655 1457. doi: 10.1002/esp

656 Struyf E, Smis A, Van Damme S, et al. (2010) Historical land use change has lowered terrestrial silica
657 mobilization. *Nat Commun* 1:129. doi: 10.1038/ncomms1128

658 Struyf E, Conley DJ (2012) Emerging understanding of the ecosystem silica filter. *Biogeochemistry*
659 107:9–18. doi: 10.1007/s10533-011-9590-2

660 Sverdrup H, Warfvinge P (1988) Weathering of primary Minerals in the natural soil environment in
661 relation to a chemical weathering model. *Water Air Soil Pollut* 38:387–408.

662 Toride N, Leij FJ, van Genuchten MT (1995) The CXTFIT Code for estimating Transport Parameters
663 from Laboratory or Field Tracer Experiments.

664 Van Ranst E, De Coninck F, Tavernier R et al (1982) Mineralogy in silty to loamy soils of central and
665 high Belgium in respect to autochthonous and allochthonous materials. *Bull la Société belge*
666 *Géologie* 91:27–44.

667 Vandevenne F, Struyf E, Clymans W et al (2012) Agricultural silica harvest: have humans created a
668 new loop in the global silica cycle? *Front Ecol Environ* 10:243–248. doi: 10.1890/110046

669 Vandevenne F and Barão AL, Ronchi B, et al (submitted) Silicon pools in human impacted soils of
670 temperate zones. *Global Biogeochemical cycle*.

671 Vanwalleghem T, Verheyen K, Hermy M, Poesen J, Deckers J (2004) Legacies of Roman land-use in
672 the present-day vegetation in Meerdaal Forest (Belgium)? *Belgian Journal Bot.* 137: 181-187.

673 Walkley A, Black IA (1934) An Examination of the Degtjareff Method for Determining Soil Organic
674 Matter, and A Proposed Modification of the Chromic Acid Titration Method. *Soil Sci* 37:29–38.

675 Watteau F, Vilemin G (2001) Ultrastructural study of the biogeochemical cycle of silicon in the soil
676 and litter of a temperate forest. *Eur J Soil Sci* 52:385–396.

677 White AF, Brantley SL (2003) The effect of time on the weathering of silicate minerals: why do
678 weathering rates differ in the laboratory and field? *Chem Geol* 202:479–506. doi:
679 10.1016/j.chemgeo.2003.03.001

680 White AF, Vivit DV, Schulz MS et al (2012) Biogenic and pedogenic controls on Si distributions and
681 cycling in grasslands on the Santa Cruz soil chronosequence, California. *geochim. Cosmochim.*
682 *Acta* 94: 72-94.

683 Zysset M, Schindler PW (1996) The proton promoted dissolution kinetics of K-montmorillonite.
684 *Geochim Cosmochim Acta* 60:921–931. doi: 10.1016/0016-7037(95)00451-3

685

686

687 **Table captions**

688 Table 1: Selected soil properties for the sampled soil horizons. Ranges were given for oxalate
689 extracted Al and Fe, pH and soil organic carbon (SOC). If only one value was give, the parameter was
690 constant. Average grain size distributions are presented for the horizons of interest. Luvisols were
691 analysed by Vandevenne and Barão (submitted) and Cambisols by Clymans et al. (2011) and Barão et
692 al. (2014).

693 Table 2: Results of different Si extraction methods for the horizons of interest as well as the
694 corresponding soil density in the columns. AkExSi stands for alkaline extracted Si according to the
695 method of Koning et al. (2002), Si_{oxalate} stands for oxalate extracted Si and Si_{CaCl₂} stands for CaCl₂
696 extracted Si. Ranges were given except when the parameter was constant. Luvisols were analysed by
697 Vandevenne and Barão (submitted) and Cambisols by Clymans et al. (2011) and Barão et al. (2014).

698 Table 3: Minimum and maximum values of pH and element concentrations measured in the effluents
699 of all columns.

700 Table 4: Average Si flux ($\mu\text{mol/d}$) and Si flux ratio (equation 2) for both horizons of forest and arable
701 land uses and in all sites.

702

703

704 **Figure captions**

705 Figure 1: Normalized Si concentrations (equation 1) measured in the effluents of the topsoils (dots)
706 and deep soils (triangles) for the forest (black) and arable land (white) plotted against pore volume.
707 Note that the scale of the y-axis differs for the two sites. Figure 2: Average initial (left axes – green
708 symbols) and final (right axes – black and white symbols) Si_{norm} ($mg.g^{-1}$) plotted versus BSi ($mg.g^{-1}$ –
709 above) and P*Si* ($mg.g^{-1}$ - below) for all horizons.

710 Figure 3: Normalized Si concentrations versus pH of the effluents for Af (dark dots), Bf (dark triangles)
711 as well as for Ac (light dots) and Bc (light triangles) in the Luvisol (grey scale) and Cambisol (black-
712 white) sites.

713 Figure 4: Boxplots of the Si concentrations (ppm) measured at two fluxes (Low: $0.8 \pm 0.2 \text{ cm d}^{-1}$; High:
714 $2 \pm 0.28 \text{ cm d}^{-1}$) for the Luvisol (lv) and Cambisol (cb) A (BSi) as well as B horizons (P*Si*). Note that the
715 scale of the y-axis differs for forest and cropland.

716 Figure 5: Correlation between the flux ratio and BSi amount (above) and the average pH (below) of
717 all soil horizons. A high flux ratio is observed when the system is near equilibrium.

718 Figure 6: Comparison between logarithmic values of r (equation 3), k_1 (equation 6), k_2 (equation 7)
719 and k (equation 8) for all soil horizons at the beginning (i) and end (f) of the experiment. Above:
720 Luvisol soils; Below: Cambisol soils. Forest: grey; Arable land: white. A horizons: dots; B horizons:
721 triangles.

722 Figure 7: Comparison of initial (green symbols) and final (black and white symbols) dissolution rates
723 ($\text{mol Si g}^{-1}\text{d}^{-1}$) for all horizons with dissolution rates of soil clay minerals (Köhler et al.; 2003; 2005;
724 Golubev et al. 2006), primary mafic silicates (Golubev et al. 2005), feldspars (Goddéris et al. 2006)
725 and phytoliths (Frayse et al. 2009) plotted versus pH. Mass normalized dissolution rates were
726 recalculated for primary minerals assuming specific surface area of $0.100\text{m}^2/\text{g}$ for 100–200 μm size
727 fraction and with $80\text{-}100\text{m}^2/\text{g}$ for clays (after Frayse et al.; 2009).

728 Figure 8: Concentrations of Si (mg l^{-1}) released from the Luvisol (above) and Cambisol (below) Af soils
729 against the leached water volume (ml). The grey zones correspond to the Si amount released by BSi
730 present in the A horizons.

731 Figure 9: Si concentrations (ppm) in the Ac_{iv} versus the leached water volume (ml) with Si amount
732 released by BSi present in the A horizons (grey zone).

733 Figure 10: Average Si flux ($\mu\text{mol/d}$) at the start of the experiment (F_{BSi} , green curve) and average
734 mineral flux (F_{min} , black curve) calculated at Q_1 for forest (left), agricultural (low intensity: middle –
735 intensive: right) land uses plotted against the soil pH for the A (top panel) and B (bottom panel)
736 horizons. The water passing through the A and B horizons (dashed blue arrow) could dissolve mineral
737 (square), biogenic (oval) and/or pedogenic Si (irregular shape). The Si sources of dissolved Si were
738 drawn in black.

739

740