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1	Release of labile Si from forest and agricultural soils
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29 Abstract

30 Despite the importance of silicon (Si) as benefecial nutrient for many plants, including 31 economically-important cereals, the reactivity of various Si pools in soils (silicate minerals, 32 amorphous compounds, phytoliths, organic litter) is not fully quantified which does not allow predicting the capacity of agricultural or forested soil to provide soluble Si to soil porewaters 33 34 where it can be used by plants. Towards better understanding of factors controlling 35 bioavailable Si in soils, here we quantified the release rate of Si from several pairs of French 36 forest and agricultural topsoils, developed on calcareous or loess parent material. We used mixed-flow and column reactors, in acetate and carbonate buffers and distilled water, at 37 38 various pH (4 to 8) and time of reaction (day to month).

39 The rate of Si release from soil (R_{Si}) exceeded that of crystalline clay minerals by 1 to 2 orders of magnitude, being 5 to 10 times lower than that of various allophanes. The rates were 40 weakly dependent on pH (compared to clays or phytoliths) and varied from 5×10^{-7} to 2×10^{-6} 41 $mol/g_{soil/day}$ at 4 < pH \leq 8. In terms of Si reactivity, four studied soil groups followed the 42 order: "calcaric cambisols \approx hypereutric cambisols \geq luvisols \geq albeluvisol". Calcaric and 43 44 hypereutric cambisols as well as luvisols exhibited a weak decrease of R_{Si} with pH increase. 45 The rate of Si release from albeluvisol increased 2 times with a pH increase from 4 to 8. There was no measurable difference in R_{Si} between agricultural and forest soils. 46

The pool of labile Si in forest soils was quantified via soil column flow-through experiments. The breakthrough curves of Si demonstrated high concentrations (1.6 to 5.7 mg/L) over first several hours of reaction in the soil column. The water leachable Si pool ranged from 0.04 to 0.08 mg Si g_{soil}^{-1} , corresponding to labile Si stock in the 0-20 cm soil of 80 to 160 kg ha⁻¹. These values can meet the annual requirements of plants in forests and cultivated soils. The pool of labile Si correlated (R_{Pearson} >0.90; p < 0.05) with Si associated with amorphous Fe and Al compounds and soluble bioavailable Si extracted using CaCl₂ 54 method, but negatively correlated with total Si content in soils and Si of phytoliths. The main 55 pools of soil labile Si could be allophanes, organo-Fe-Al-Si compounds and adsorbed forms 56 of Si onto Fe and Al hydroxides. We hypothesize that, because of low sensibility of R_{Si} to type of soil and fluid pH, the majority of soils regulate Si release at some 'universal' rate 57 58 which is further reflected in relatively narrow range of riverine Si concentrations and export 59 fluxes across the world. Therefore, the modeling of chemical weathering and element export 60 flux in the watersheds should incorporate the experimentally measured reactivity of the whole 61 soil rather than individual constituting primary or secondary minerals.

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1. Introduction

Silicon is not seen as an essential element for plants, but many studies have 65 66 documented that it is a beneficial element for many crops (Coskun et al., 2019). Low level of 67 bioavailable Si has become an issue especially for cultivated soils naturally or anthropically 68 depleted in plant available Si (Tubana et al. 2016; Haynes, 2017). The characterization of 69 bioavailable soil Si is still empirical and the knowledge of fundamental mechanisms that drive 70 the biogeochemical cycle of silica under cultivation are necessary for a better assessment of 71 the impact of Si on plant development (Cooke and Leishman, 2016) as well as the future 72 impact of global change on the Si cycle (Schaller et al., 2021; Yang et al., 2019, 2020).

There are several main reservoirs of Si in soils that can be used by plants provided that the Si leaching from these solid phases to the interstitial porewater is fast enough. First, these are primary and secondary crystalline silicate minerals that constitute the bulk of bottom and intermediate soil horizons. The reactivities (dissolution rates) of most Si-bearing primary and secondary alumosilicate minerals commonly present in soils and quartz are quite low (Schott et al., 2019) and not capable of providing sufficient amount of labile Si required for plant 79 growth, especially when the state of weathering is well advanced (de Tombeur et al., 2020). 80 Possible exceptions are soils developed on highly reactive materials such as volcanic ash 81 (Ugolini and Dahlgren, 2002; Vandekerkhove et al., 2016) or wollastonite (Cho et al., 2010). 82 Amorphous materials, including biogenic silica (mainly phytoliths) and short-range order 83 minerals have been identified as another potential source of dissolved Si (Puppe, 2015; 84 Meunier et al., 2017; Cornu et al., 2022; Li et al., 2022). The reactivity of plant phytoliths is quite high, greatly exceeding that of clay minerals (Fraysse et al., 2009). The uptake of Si 85 86 from phytoliths allows the plants to overcome labile Si deficit as it is established in various 87 cultivated and pristine environments (Desplanques et al., 2005; De Tombeur et al., 2020; 88 Gérard et al., 2008). Finally, the plant litter itself, where Si is present as both phytoliths and 89 the dispersed form (Watteau and Villemin, 2001; Watteau et al., 2002; Fraysse et al., 2010), 90 and Si which is bound to organic compounds (Kolesnikov and Gins, 2001), including humic 91 acid-Al-Si complexes (Merdy et al., 2022) represent another potentially labile pool of Si for 92 plants. For example, in the Amazonian forest, the Si input from the litterfall on top of the soil 93 is about four times greater than the Si leached out of the system (Lucas et al., 1993).

94 In most soils, the Si pool available for plants may comprise all the reservoirs listed above. In addition, some Si can be adsorbed on the surfaces of soil minerals and organic debris 95 96 and thus can be easily mobilized to aqueous solution (Rückert, 1992; Brinkman, 1970). 97 However, aggregates in the soils may slower the process of dissolved Si mobilization (Li et al., 98 2022). So far, plant available Si (PAS) has been empirically estimated by chemical procedures 99 using extractants such as 0.01 CaCl₂ (i.e., Haysom and Chapman, 1975) that provide a positive 100 correlation with plant yield (Babu et al., 2016; Narayanaswamy and Prakash 2010). Various 101 PAS quantification methods demonstrated positive correlations with factors that may affects Si 102 availability, such as pedological and geological conditions (Landré et al., 2020), soil pH 103 (Meunier et al., 2018; Caubet et al., 2020; Schaller et al., 2021), weathering stage (Klotzbücher

104 et al., 2014) and the presence of phytoliths (De Tombeur et al., 2020) and clay fraction and 105 short-range ordered (SRO) aluminosilicates (e.g. allophanes and imogolites; Caubet et al., 106 2020; Cornu et al., 2022; Keller et al., 2021). Cornu et al (2022) found that PAS based on the 107 CaCl₂ method was generally higher in cultivated soils than in forest soil and was controlled by 108 pH and the presence of allophanes. However, the PAS methods do not allow to propose general 109 laws of Si release rate. For this, laboratory experimental approaches are needed. Thus, Barao et 110 al. (2019) used kinetic batch experiments with Belgium soils and found that reactivity of Si in 111 croplands were higher than that of forest and pasture soils. Ronchi et al. (2015) used a leaching 112 test approach on soil column to evaluate the dissolution rate of Si and to compare it with that of 113 single soil minerals and biogenic Si pools. They found that the Si release from Belgian 114 Luvisols and Sweden Cambisols are controlled by pH and decline from forest to cropland while 115 PAS (CaCl₂ method) showed an opposite trend. Accordingly, more data is required to 116 disentangle the significance of rate dissolution laws in soils and the impact on cultivated lands.

117 Building on this information, the purposes of this study are twofold. First, we aimed at 118 assessing the rates of Si release from French temperate soils developed from calcareous or 119 loess parent materials (characterized by Cornu et al., 2022), collected in adjacent cultivated and 120 forest plots. Specifically, we intended to quantify the impact of solution composition (pH, 121 presence of organic ligand or bicarbonate ion) on Si release rate in dynamic experiment and to 122 compare Si release rate from various soils to that of clay minerals and Si-bearing amorphous 123 compounds. Secondly, we focused on measuring initial, non-stationary Si release from soil, 124 allowing to quantify the pool of most labile soil Si in order to relate it to conventionally-125 measured forms of Si in soils. In this regard, the present work is devoted to identify the 126 physico-chemical (abiotic) factors controlling dynamic Si pool in soil. Furthermore, it allows 127 quantifying possible bioavailable pool, rather than characterizing real bioavailability of silicon.

For the latter, specially designed mesocosm-level experiments with Si uptake by live plants andanalysis of Si concentration in the biomass are necessary.

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132 2. Materials and Methods

133 We have chosen seven French soils developed in calcareous or loess parent material in 134 the temperate climate zone: 2 hypereutric cambisols (called 'calcisol' for brevity), 2 calcaric 135 cambisols ('calcosol'), 2 luvisols, and 1 albeluvisol (WRB, 2006 soil classification; 136 Chesworth et al., 2008). Their basic physical and chemical properties are listed in Table 1 and 137 more information is provided in Cornu et al. (2022). We used a paired site approach which 138 includes adjacent soils with identical pedological factors (topography, parent material, climate 139 and age) but different in their land use (cultivated versus forest soils). Localization of sampled 140 soils is illustrated in Supplementary Figure S1. The soils were air dried, sieved through 2 mm 141 sieve and sterilized prior to using for dissolution experiments. Specific surface area was 142 measured using multiple point N₂ adsorption (Micrometrics ASAP 2010 apparatus) after 143 degassing during 48 h at 120°C.

144 The experimental setup involved two independent dynamic (flow-through) reactors, operating at high and low ratio of fluid to soil (Fig. 1). In order to measure Si release rate 145 146 from soils as a function of solution pH, at high fluid : solid ratio, we used classic mixed-flow 147 reactor (Fig. 1 A), developed for measuring the dissolution rates of individual minerals (i.e., 148 Pokrovsky et al., 2009, 2021; Schott et al., 2009). Similar reactors were used for assessing the 149 Si-based reactivity of soil clay minerals (i.e., Köhler et al., 2003, 2005; Golubev et al., 2006), 150 plant phytoliths (Fraysse et al., 2008, 2009) and whole plant litter (Fraysse et al., 2010). These 151 reactors allow measuring steady-state Si release rate at fixed pH and other solution 152 parameters. Steady-state dissolution rates were obtained at distinct solution compositions and

153 pH at a constant temperature of $25.0 \pm 1.0^{\circ}$ C in a thermostated room. Reacting fluids were 154 comprised of deionized degassed H₂O, Merck reagent grade HCl, NaOH, NaHCO₃, NaCH₃COO, and NaCl. All solutions were prepared from 18 MΩ ultrapure sterile water 155 156 (MilliQ Plus system) having a blank of dissolved organic carbon < 0.05 ppm. The input fluid 157 was stored in a polyethylene container protected against CO₂ uptake from the atmosphere. It 158 was injected into the reaction vessel using a Gilson® peristaltic pump at typical flow rates 0.1 mL min⁻¹. The reactor consisted of a 25 mL Teflon vessel which was continuously stirred 159 160 with a floating Teflon supported magnetic stirrer, which prevented soil grinding during 161 experiments. The reactive solution left the reactor through a series of 2.5 µm polycarbonate 162 and 0.45 µm Nylon filters mounted in a row. All reactors initially contained 1.50 g of soil. 163 The experiments started from injecting into reactor the Milli-Q water at pH = 5.6, followed by 164 a mixture of 10 mM NaCl and 1 mM NaHCO₃ at pH = 8, and a mixture of 5 mM NaCl and 5 165 mM Acetic acid at pH = 4.2. The duration of each run ranged from 200 to 500 h. Finally, the 166 reactor was run again with Milli-Q at pH around 6 during 450 h. For most experiments lasting 167 40-60 days in total, one sampling per day was performed. The total mass of soil in the reactor 168 was measured at the beginning and at the end of experiment; no sizable changes (i.e., within 169 10 %) have been detected.

170 Steady-state dissolution rates (R_{Si} , mol g_{soil}^{-1} d⁻¹) were computed from measured 171 solution composition using Eqn. 1:

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$$R_{Si} = -q \cdot [Si(aq)]_{\text{outlet}} / m \tag{1}$$

173 where q (L s⁻¹) designates the fluid flow rate, $[Si(aq)]_{outlet}$ (mol L⁻¹) stands for the outlet Si 174 concentration (M), and m (g) refers to the total soil mass of soil present in the reactor, 175 respectively. Uncertainties on the steady-state rate constants are dominated by the uncertainty 176 on the standard deviation on average Si a concentration at the steady-state (±10-20 %).

177 The second type of approach involved flow-through column experiments used for 178 evaluating water-labile pool Si in soils (Fig. 1 B). Similar column experiments were shown to 179 be efficient for measuring flux of Si from soils and assessing Si release rate at close to 180 equilibrium conditions, at high soil : fluid ratio, most pertinent to natural settings (Ronchi et 181 al., 2015). This setup involved small polypropylene column (diameter 1 cm, length 5 cm) 182 packed with sieved (< 2 mm) soils. The column was filled with 1 g of upper 0-10 cm horizon 183 of forest soil (F1) and 3 g of lower 20-30 cm horizon of forest soils (F2); we used hypereutric 184 cambisol, calcaric cambisol and luvisol for these experiments. Fine soil sample (< 2 mm) was 185 placed on the top of Teflon cotton supported by a porous ($< 500 \mu m$) Teflon disk; the outlet of 186 the column was fitted with a 0.45 µm filter, and the fluid flow direction was from the bottom 187 to the top. Similar to mixed-flow reactors, three inlet solutions were used in column 188 experiments: Milli-Q water at pH = 5.6, a mixture of 10 mM NaCl and 1 mM NaHCO₃ at pH 189 = 8, and a mixture of 5 mM NaCl and 5 mM Acetic acid at pH = 4.2. Continuous 190 breakthrough curves of solutes were monitored from specific conductivity and pH 191 measurements of the outlet fluid. These allowed integrating the amount of Si released from 192 soil column as a function of time and over full duration of experiments. Similar approach for 193 identifying the labile Si pool was used in batch experiments of other studies (e.g., Barao et al. 194 2019). Because the concentration of Si in the column outlet solution strongly decreased over 195 the first 10-100 h to some steady-state concentrations (see section 3.2 below), while the pH 196 was buffered by acetate or carbonate buffer, the labile (fast leachable) pool of Si in soil 197 sample was calculated for discrete time interval (0-10 h and 10 - 100 h). For this, we 198 numerically integrated the amount of released Si with 1 to 2 h step for the 0-10 h period and 199 with 10 to 20 h step for the 10-100 h period and normalized the mass of released Si to the 200 total amount of soil in the column.

The pH in the outlet solution was measured using a combination glass electrode (Mettler Toledo) calibrated with NIST buffers (pH 4.01, 6.865, 9.18 at 25°C), with an uncertainty of \pm 0.01 units. Aqueous silica concentration was determined using Quadripole ICP MS Agilent 7500 ce, with an uncertainty of 2% and a detection limit of $3.6 \cdot 10^{-7}$ M. The quality of measurements was monitored by regular analysis of SLRS-5 certified sample (2.2 mg L⁻¹ Si) and an in-house standard of 0.01 M NaCl with ten times lower Si concentration.

207 Statistical treatment of the data included mean values and their standard deviations (in 208 case of replicates and for calculating the steady-state concentrations from 4 to 5 sampling 209 points) and linear regressions. Pairwise (Pearson) correlations were used to assess the 210 relationship between various forms of Si in soils as measured by standard techniques (e.g., 211 Cornu et al., 2022) and the labile Si pool measured in the experiments. Further, a pairwise 212 comparative analysis was run via non-parametric Mann-Whitney test (U-test) to detect the 213 differences between Si release rate or Si pools in datasets of different soils. The level of 214 significance was fixed at 0.05 (95% confidence level) to consider a result as statistically 215 notable. All plots were built using MS Excel 2016 and the Statistica-12 software package 216 (http://www.statsoft.com).

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219 **3. RESULTS**

220 3.1. Long-term dissolution in mixed-flow (open) reactors

Results of 16 long-term (10 - 15 days each) soil dissolution experiments are listed in Table 2 and illustrated in **Fig. 2** for two forest and two agricultural soils. The steady state outlet Si concentrations were typically achieved after first 20 h corresponding to 5 residence times of the fluid in the reactor. In this regard, the chemical and mechanical steady-state were similar. The outlet Si concentration responded to the change of chemical composition and the pH of the inlet fluid. Silica concentration increased in the order "Milli-Q (pH = 6.0 - 6.5) < 0.01 M NaCl/NaHCO₃ (pH = 8.0 ± 0.2) < 0.01 M Na Acetate (pH = 4.2 ± 0.1)". After 800 h of experiment, we injected again the MilliQ water, and in most cases, the outlet concentration of Si were within ±20-30% of the values obtained at the beginning of experiment.

230 The Si release rates ($R_{\rm Si}$) calculated from steady-state outlet Si concentration (Eqn. 1) 231 presented a weak dependence on solution pH which was, however, depended on the type of 232 soils (Fig. 3). The hypereutric cambisol $R_{\rm Si}$ decreased by a factor of 1.6 when pH increased 233 from 4.2 to 6.5, had a minimum at pH 6.5 and then stabilized at pH close to 8 (Fig. 3 A). The 234 calcaric cambisol R_{Si} decreased by a factor of 2±0.5 from pH 4.2 to 7-8 (Fig. 3 B). The luvisol 235 R_{si} exhibited a minimum at pH around 6 (Fig. 3 C). Finally, the albeluvisol stood apart from 236 all other soils and yielded a 2-fold increase in $R_{\rm Si}$ when the pH increased from 4.1 to 8.2 (Fig. 237 **3** D). None of the studied soil yielded significant (Mann-Whitney test, p < 0.05) difference in 238 Si release rate between forested and cultivated soils. The plot of all soils in log Rsi scale 239 demonstrated overall weak dependence on pH (Fig. 4). When normalized to specific surface 240 areas, the rates of Si release from various soils exhibited the order 'hypereutric cambisol < 241 luvisol < calcaric cambisol ~ albeluvisol' (Table 2; Fig. S2 of the Supplement).

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244 3.2. Silicon leaching from soils in the column reactor experiments

The rates of Si release from forest soils were calculated from the Si concentration at steady-state (typically after 10-100 h of reaction) in the column experiments using Eqn. 1. The rates measured in column reactors are listed in **Table 3**. The rates ranged from 1.0×10^{-6} to 1.9×10^{-7} mol Si g⁻¹ day⁻¹ for 800 to 150 µg L⁻¹ of dissolved Si output concentration. These values are fairly comparable with R_{Si} measured in mixed-flow reactors, when the ratio soil : fluid was one order of magnitude higher.

At the same time, the initial outlet Si concentrations over first 4 hours were very high, 251 ranging from 4000 to 8000 μ g L⁻¹ (**Fig. 5**). Specifically, the outlet Si concentrations decreased 252 from 6000 to 1000 μ g L⁻¹ over 10 h reaction with hypereutric cambisols, from 4000 to 1000 253 μ g L⁻¹ over 7 h for calcaric cambisol and from 8000 to 500 μ g L⁻¹ over 6 h with luvisol. The 254 initial outlet Si concentrations corresponded to instantaneous, non-steady state R_{Si} around 10⁻⁵ 255 mol Si g⁻¹ day⁻¹. This is an order of magnitude higher than the rates at the steady state 256 257 measured in both mixed-flow reactor and column experiments. The numerical integration of 258 the breakthrough curve (i.e., Si concentration vs time over first 0-10 h of reaction) in the Milli-Q water allowed quantifying the pools of labile Si, equaled to 0.08 ± 0.01 mg Si g soil⁻¹ 259 for hypereutric cambisols and 0.040±0.002 mg Si g soil⁻¹ for luvisols. These numbers were 260 261 calculated from the average of two samples for each soil (1166 (F1+F2) and BS2 (F1+F2) of 262 hypereutric cambisol; 340 (F1+F2) and 62 (F1+F2) of luvisol). The calcaric cambisols 263 demonstrated much longer tail of high outlet concentrations, persistent over 90 h of reaction; the overall labile Si for calcosoil 755 F1 is estimated as 0.145±0.02 mg Si g soil⁻¹, although 264 265 the actual uncertainties may be much higher. This particular behavior of calcosol could be 266 linked to progressively dissolving carbonate mineral grains that buffered the release of Si 267 from relevant silicate pools.

For calcaric cambisol and hypereutric cambisol, approximately half of the labile pool was mobilized over first 0-10 h of reaction (**Table 4**). In contrast, > 90 % of labile Si pool in the luvisol was released over first 4 h of reaction or even faster, given insufficient temporal resolution at the beginning of experiments. This difference can be tentatively linked to the fact that the cambisol had much higher quantity of clay minerals compared to the luvisol.

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3.3. Testing the link between experimental Si release rate, labile Si pool and analytical
Si pools in soils

276 Based on recent study of various conventional analytical pools of Si in soils (Cornu et 277 al., 2022, see their **Table 1**), we tested a correlation of these pools with experimentally 278 measured Si release rates in mixed flow reactors and labile Si pools measured in the column 279 experiments. For this, we used steady-state R_{Si} values from mixed-flow (Table 2) and flow-280 through column (Table 3) experiments, and pools of labile soil Si integrated over 0-10 and 281 10-100 h of reaction in column experiments at various pH (**Table 4**). In the latter case, the 282 reason for considering independently these two time intervals is that they could correspond to 283 two pools of leachable Si, as seen from the relevant breakthrough curves (Fig. 5). In contrast, 284 after 100 h of reaction, there are steady-state Si release processes that can be better reflected 285 by a stationary Si release rate (R_{Si}). There was no significant (at p < 0.05) correlation between 286 Si release rate neither in mixed flow nor column reactor, and any conventional analytical 287 forms of soil Si, including content of total Si, oxalate-, CaCl₂-, and dithionite-extracted Si and 288 phytoliths in studied soils (Table S1 and Fig. S3 of the Supplement). However, the pools of 289 labile Si quantified from column experiments on forest soils exhibited significant correlations 290 (p < 0.05) with certain labile Si forms in soils (Table 5). The strongest correlations (R² = 291 0.94-0.98, p < 0.01) were observed between Si pool mobilized over 10-100 h reaction in the 292 Milli-Q water or over 0-10 h in the acetate buffer and Si concentration in the form of 293 allophones/imogolites as extracted by Tamm method (Si_0), which provides amorphous Fe/Al 294 compounds (Fig. 6 A, B). The pool of labile Si released over 10-100 h in the acetate buffer 295 strongly ($R^2 = 0.97$, p < 0.01) correlated with Si_{CaCl2} forms in soils (soluble, bioavailable Si 296 extracted with CaCl₂), Fig. 6 C. Note that the correlations of different Si forms in soils 297 determined in Cornu et al. (2022) with total (0-100 h) leachable pool of Si determined in 298 column experiments were much lower than those for two fractional pools (0-10 and 10-100 299 h). The total chemical pool of Si in soils (Si_{tot}) strongly ($R^2 \ge 0.94$, p < 0.01) anti-correlated with both acetate- and Milli-Q reacting pools determined in column experiments (Fig. S4 ofthe Supplement).

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305 4. DISCUSSION

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4.1. Comparison of Si release rate between bulk soil, minerals, and phytoliths

A comparison of whole soil Si release rates with dissolution rates of common soil 307 308 minerals and plant phytoliths measured in the mixed-flow reactor similar to the one used in 309 this study is given in Figure 4. Added to this figure also the recent data for allophane 310 dissolution in batch reactors (Ralston et al., 2018) and results of column leaching experiments 311 on forest soils (Ronchi et al., 2015). Noteworthy that all soils except albeluvisol at pH 4.2 312 exhibited sizably higher (1-2 orders of magnitude) Rsi values compared to those of typical 313 clay minerals present in soil. Whilst in acidic environment (pH = 4.0-4.5), the rates of Si 314 release from the whole soil are 2 to 10 times higher than those of soil clay minerals, at pH = 6315 to 8.5 the difference sizably increases because the clay minerals decrease their rates with pH 316 between 4 < pH < 7.5. At the same time, this trend of R_{Si} with pH qualitatively corresponds to 317 that observed for luvisols and hypereutric cambisols (calcisol) in Fig. 3. In contrast, the Rsi of 318 French soils developed in calcareous or loess parent material stay essentially constant at (10 \pm 5) × 10⁻⁶ mol Si /g_{soil}/day, or (8 ± 3) × 10⁻⁸ mol Si /m²_{soil}/day. The calcaric cambisol (calcosol) 319 320 and albeluvisol exhibited a different trend of R_{Si} with pH (Fig. 3). The dissolution rate of 321 albeluvisol increases with pH, which is also observed for quartz given the importance of the 322 quartz fraction in this type of soil, including the $< 2 \mu m$ fraction (i.e., 60 % of the crystalline 323 silicates, Cornu et al., 2022). However, the mass-normalized Si release rate from quartz is several orders of magnitude lower than that from studied soils, and the slope of $\log R_{Si} - pH$ 324

dependence for quartz is much higher than that observed for albulivisol (factor of 2 and 0.5 per one pH unit, respectively). Furthermore, the luvisol also contains sizable amount of quartz but did not yield an increase in $R_{\rm Si}$ with pH. For the calcaric cambisols (calcosol), there is a constant decrease of the dissolution rate with the pH. This could be due to a dissolution of the carbonate fraction in the first stage of the experiment.

330 Overall, at pH around 7-8, the difference in Si release rate between typical soil clay 331 minerals and whole soils reaches more than 1.5-2.0 orders of magnitude. This is rather 332 unexpected result, given that the synthetic clays (kaolinite, illite, chlorite and smectite) used 333 for this plot constitute the majority of soils studied in this work (e.g., Cornu et al., 2022). 334 However, one should be careful when performing such a comparison: individual clays used in 335 previous experiments are generally better crystalline and larger than those encountered in 336 soils. As a result, the mass-normalized reactivity of natural soil clays may be higher than 337 those of synthetic crystalline minerals, as also demonstrated in some mineral bag natural 338 experiments (e.g., Cornu et al., 1995).

339 The Si release rates from the whole soil measured in this study are drastically different 340 from those of plant phytoliths as also shown in **Fig. 4**. Not only the plant phytoliths are 1 to 3 341 orders of magnitude more 'reactive' than soils (Fraysse et al., 2009), but the shapes of $\log R_{Si}$ 342 - pH dependences between soils and phytoliths are totally different. Taken together, negligible 343 role of phytoliths in Si supply to aqueous solution in experimental reactors and column-344 through experiments of the present study is demonstrated by lack of correlations (or negative 345 correlations) between the labile Si pool and phytoliths content in forest soils (Table 5), and 346 totally different pattern of rate dependence on solution pH for studied soils and plant 347 phytoliths (Fig. 4). As such, the reactivity of Si in soils investigated in this study cannot be 348 explained by a presence of small fraction of highly reactive phytoliths. In contrast to 349 phytoliths, the plant litter exhibits quite weak dependence of R_{Si} on pH; for 6 various plants, the Si release rate ranged from 10^{-7} to 10^{-5} mol g_{plant}^{-1} d⁻¹ with very weak increase in R_{Si} with pH increase (ca., 0.3 log *R* unit per 5 pH unit, Fraysse et al., 2010). However, it is very unlikely that the presence of small (1-10%) amount of fresh, Si-rich plant litter in studied soils can explain their reactivity in aqueous solution: the content of refractory organic matter in soils is too low and highly variable among soils (10 to 70 g kg⁻¹, see **Table 1**) to allow a realistic impact of admixture of plant litter/soil humic material as a source of Si in aqueous solution contacting with soil in our experiments.

357 To get further insights into mechanisms driving Si release from soils in our 358 experiments, we consider several possible pools of Si. First, in addition to poorly reactive 359 quartz, these are 'primary' crystalline clays (kaolinite, illite, chlorite) and secondary, poorly 360 crystalline smectites and/or interlayered illite-smectite minerals (Cornu et al., 2022). Second, 361 there are amorphous/poorly crystalline imogolites and allophanes, including organo-alumino-362 siliceous, organo-Fe-Al-siliceous compounds (Farmer et al., 1980; Matichenkov and Snyder, 363 1996; Ralston et al., 2021). While the dissolution of 'usual' clays cannot provide the observed 364 magnitude and pH-dependent pattern of R_{Si} , the reactivity of amorphous Si-bearing mineral 365 and organo-mineral compounds such as pure end-member allophanes, including both Fe-free 366 and Fe-rich compounds (i.e., Ralston et al., 2021) is an order of magnitude higher than that of 367 soils studied in this work (see **Fig. 4**) and thus allophane cannot be excluded as a source of Si 368 released from soils. An indirect evidence of the importance of this pool of soil Si in the short-369 term Si release patterns in our experiments is strong positive correlation observed between the 370 labile Si assessed in column filtrations and Si_O measured by Tamm extraction procedure, and 371 Si extractable by CaCl₂ (**Table 5, Fig. 6**). This is consistent with a similarity of the R_{Si} – pH 372 dependence between allophanes and the calcaric cambisol, the soil in which allophane are the 373 most present.

374 It has been known for long that silicic acid is readily adsorbed by and released from 375 soils and soil minerals (Beckwirth and Reeve, 1963, 1964; McKeague and Cline, 1963; 376 Haynes and Zhou, 2020). Therefore, the third major pool of soil Si is siliceous acid and 377 silicate ions, adsorbed onto surfaces of soil minerals, first of all Al and Fe oxyhydroxides 378 (Bruun Hansen et al., 1994; Hingston and Raupach, 1967). In particular, strong adsorption of 379 Si onto Fe(OH)₃ is fairly well known (Dietzel et al., 2002; Vempati and Loeppert., 1989). The 380 adsorption/desorption rate of silica from solid surfaces is usually very fast, and the 381 equilibrium is established over the order of first hours (Beckwirth and Reeve, 1963, 1964). 382 The majority of Si adsorbed on the surface of ferrihydrite and goethite at room temperature 383 occurred over first 50 to 100 h (Delstanche et al., 2009). As such, the initial high Si 384 concentration in flow-through column experiment can stem from mobilization of adsorbed Si 385 pool. Consistent with this possibility is the observation that the reversible adsorption (and, 386 consequently, desorption) of silicic acid onto/from Fe hydroxide is independent on pH at $5 \le$ 387 $pH \le 8$ (Sigg and Stumm, 1981).

388 Finally, a sizable pool of Si in soils may be represented by biogenic silica such as 389 phytoliths, diatom frustules and exo-skeletons of protozoe (Sommer et al., 2006). The 390 dissolution of this bulk biogenic silica, however, cannot provide the observed pH-independent 391 pattern of Si release from soils studied in this work. In contrast to 'classic' phytolith such as 392 those investigated by Fraysse et al (2006, 2009), small size phytogenic silica ($< 5 \mu m$, by 393 definition proposed in Sommer et al., 2006) has not been investigated from the view point of 394 its reactivity in aqueous solution. However, it is unlikely that both the magnitude and pH-395 dependence of small size phytogenic R_{Si} would be different from those of phytoliths: the grain 396 size has no sizable impact on surface-normalized mineral dissolution rates, unless these 397 minerals were subjected to strong shock which can generate dislocations (e.g., Schott et al., 398 2009). The same is true for abiotically formed amorphous silica which is known to precipitate from soil solution in the form of pure phases on mineral surfaces (Drees et al., 1989): the strongly pH-dependent pattern of amorphous silica dissolution rate is different from much weaker pH dependence or even pH-independent pattern of Si release from soils, studied in this work.

403 We observe a sizable, about two orders of magnitude, difference in Si release rate 404 measured for the French soils in the mixed-flow reactor in this study and the rates of Si 405 leaching in column experiments with forest and arable Swedish cambisols and Belgian 406 luvisols reported by Ronchi et al. (2015), Fig. 4. We tentatively explain this difference by 407 first, more important role of allophanes and less important role of clay minerals in controlling 408 Si release from studied soils compared to cambisols and luvisols of Ronchi et al. (2015). Note 409 that, although the rates of Si release from luvisol and hypereutric cambisol decrease with pH 410 similar to that of Ronchi et al. (2015), the R_{Si} measured in this study are 2.0±0.5 orders of 411 magnitude higher. Second, a lack of pH-dependence for Si release rate from soils in this study 412 (notably of calcaric cambisol and albeluvisol) and similarity of Si release rate in Ronchi et al 413 (2015) with common soil clays suggest the dominance of different mineral pools determining 414 the Si release pattern. In particular, we noted an order of magnitude higher Si_{oxalate} content in 415 the soils of this study compared to those of Ronchi et al. (2015). Moreover, the initial outlet Si 416 concentration in experiments of Ronchi et al. (2015) was > 10 times higher than that in the present study and it achieved 50 to 70 mg L^{-1} . At such high concentrations, the Si release 417 418 becomes limited by solubility of amorphous silica (SiO₂ \times *n*H₂O). It is thus possible that 419 mixed-flow reactors with high fluid:solid ratio, used in this study and the column reactors 420 with very low fluid:solid ratio of Ronchi et al (2015) do not probe the same pools of soil Si, 421 despite similar time scale used to extract the steady-state rates. Another possible explanation 422 could be linked to different nature and relative abundances of crystalline clays and short range 423 ordered minerals in soils used by these two studies.

425

4.2. Si release from soils in natural settings

426 Regardless of exact chemical and mineralogical nature of leachable Si pool in the 427 studied soils, the main consequence of the presence of this labile Si is that it can be quickly, 428 on the order of hours or even minutes, mobilized into aqueous solution (i.e., after rain 429 infiltration) and become available for plant uptake. Overall, the pool of fast (0-10 and 10-100 h) water-leachable, mobile Si in forest soil ranges, depending on pH, from 0.04 mg Si g_{soil}⁻¹ 430 for luvisol to 0.08 mg Si g_{soil}^{-1} for hypereutric cambisol and calcaric cambisol (**Table 4**). 431 432 Assuming that only upper 0-20 cm layer of soil reacts with aqueous solution (Table 2), and considering typical soil stock (0-20 cm) of 2×10^6 kg ha⁻¹ (Winfried et al., 2018), this gives the 433 labile Si stock of 80 to 160 kg bioavailable Si ha⁻¹. This value can meet the annual (or even 434 monthly) requirements of plants in bioavailable Si (2 to 90 kg Si ha⁻¹, Cornelis et al., 2011; 435 436 Cornelis and Delvaux, 2016). In the temperate forest, Si uptake flux by deciduous trees and Douglas fir ranges from 36 to 46 kg ha⁻¹ y⁻¹, and that of the pine forest does not exceed 7 kg 437 ha⁻¹ y⁻¹ (Lucas, 2001; Gérard et al., 2008). Therefore, experimentally measured mobile Si pool 438 439 in forest soils is potentially capable of providing the totality of this demand; however, more 440 measurements on specific soils are needed to further quantify this potential.

441 The upper (0-20 cm) soil profile can be considered as a mixed-flow reactor with 442 rainwater input corresponding to annual precipitation minus evapotranspiration, or runoff of 443 the riverine watershed. Combined with the mass of soil and the rates of labile Si release from 444 bulk soil to the outlet river water, this allows determining the concentration C_{Si} :

 $C_{\rm Si} = R_{\rm Si} \times m \,/\, D \tag{2}$

446 where *m* is the mass of soil in the ecosystem (kg ha⁻¹), *D* is the flow rate or annual runoff 447 (precipitation minus evapotranspiration), in mm yr⁻¹ or L ha⁻¹, and R_{Si} is the experimental 448 dissolution rate (mol_{Si} g_{soil}⁻¹ d⁻¹). To calculate C_{Si} , we will assume typical parameters of

temperate forest at the steady-state with respect to biomass growth and decay: $m_{0.20 cm} = 200$ 449 kg m⁻² or 2×10^6 kg ha⁻¹ (Winfried et al., 2018), D = 13700 L d⁻¹ ha⁻¹ corresponding to a runoff 450 of 500 mm y⁻¹, and $R_{Si} = 10^{-6}$ mol Si $g_{soil}^{-1} d^{-1}$ corresponding to Si release rate from soil in 451 452 circumneutral solutions (pH = 5-8) measured in this study, see **Table 2** and **Fig. 4**. This yields $C_{\rm Si} = 0.15 \text{ mol } L^{-1}$ or 4100 mg Si L^{-1} , which is several orders of magnitude higher than typical 453 454 Si concentration in surface waters (4.2-5.0 mg L^{-1} , Gaillardet et al., 1999) and interstitial soil solutions of surficial horizons $(2.8 - 14 \text{ mg L}^{-1}, \text{ Sommer et al., } 2006; \text{ Pokrovsky et al., } 2005a,$ 455 456 b). Therefore, less than 1% of upper soil, receiving the incoming rainwater and releasing Si at 457 the steady-state conditions (i.e., no aggrading forest and no silica precipitation in deeper parts 458 of the soil profile) is capable to provide the observed Si concentration in surface waters.

459 An unexpected result of this study is rather similar values of Si release rate regardless 460 of soil type, agricultural use, and solution pH. Note that we could not use coupled forestcultivable soil approach for quartz-rich and clay-poor sand dunes because agricultural soils 461 462 were not available for such substrates. It is thus possible that 'universal' Si release rate 463 proposed in this study might turn out to be not so 'universal' if screened across all possible 464 soils, including clay-poor sands or ultisols (red clay soils), which are dominated by 1:1 clay 465 minerals instead of 2:1 clays studied in this work. Therefore, keeping in mind that the 466 substrates investigated in this work are only representative for well differentiated soil 467 developed on loess and poorly differentiated soil developed on calcareous soils, we can 468 extend the discussion to more general case of various lithological context. We note that the 469 natural Si export fluxes (yields) by rivers from watersheds are also similar (by an order of 470 magnitude), despite large variations in soil type, rock lithology, vegetation, runoff and soil 471 solution pH across different biomes as illustrated below. Thus, the total annual Si export 472 fluxes by rivers of boreal and temperate watersheds, although sizably dependent on runoff, 473 are within the same order of magnitude regardless of climate and lithological context (basalts,

474 granites, sedimentary rocks and even peatland environments). For example, in boreal and temperate zone, riverine Si vield ranges from 0.3 to 3.0 t Si km⁻² y⁻¹ (Oliva et al., 2003; 475 476 Zakharova et al., 2005, 2007; Pokrovsky et al., 2005b, 2020; Chupakov et al., 2020). A recent study of 20 Canadian rivers of contrasting land cover, lithology, soil type and climate 477 demonstrated a range of Si export fluxes from 0.2 to 6.6 t km⁻² y⁻¹ with an average value of 478 479 1.6 t km⁻² y⁻¹ (Phillips and Cowling, 2019). Even in fresh Hawaiian basalts, the range of Si export rate is only from 0.4 to 15 t km⁻² y⁻¹ (Derry et al., 2005), similar to silica export fluxes 480 from the rooting zone (20–30 cm depth) in these tropical settings (1.1 to 25 t km⁻² y⁻¹, Hedin 481 482 et al., 2003). A compilation of 68 watersheds on granitoid rocks at highly contrasted runoff 483 and temperatures demonstrated a Si weathering flux that ranged within less than an order of 484 magnitude (White and Blum, 1995). The magnitude of these natural variations are much 485 lower than the ranges of Si release rates in laboratory experiments on various rocks and 486 individual minerals. Indeed, the laboratory-based dissolution rates of silicate minerals (R_{Si}) 487 range over more than 4 orders of magnitude at circum-neutral pH, depending on the identity 488 of mineral (see Schott et al., 2009 and Heřmanská et al., 2022 for reviews). We therefore 489 hypothesize, that, in addition in incontestable control on Si export fluxes of transport 490 processes such as fluid residence time and flow rates (Maher, 2010) and biological processes 491 such as plant uptake and litter decay (Lucas et al., 1993; Derry et al., 2005; Gérard et al., 492 2008; Fraysse et al., 2010), the topsoil itself may exert a major "buffering" effect on Si export 493 from the watershed. By virtue of its silicate minerals, notably short-range order clays, labile 494 Si pool and low sensibility of R_{Si} to the identity of soil and fluid pH, the soils across the world 495 may regulate Si release rate at some 'universal' rate which is further reflected in relatively 496 narrow range of riverine Si concentration and export flux. The latter is primarily dependent on 497 river runoff rather than soil type and land use of the watershed.

498 In this regard, reactive transport and biogeochemical modeling of Si (and related 499 elements) cycle in the system 'rock-soil-river watershed' (i.e., Godderis et al., 2019) should 500 incorporate the reactivity of soils based on experimental data of the whole soil rather than 501 individual constituting minerals. Consideration of superposition of known dissolution rates of 502 primary and secondary soil minerals, routinely used in such modeling, instead of 503 experimentally-measured whole soil rates may underestimate Si release (and thus, relevant 504 concentrations in surface fluids) by 1 to 2 orders of magnitude. As such, experimental 505 measurements of labile Si in various soils across the world, using flow-through reactors with 506 both soil powder and soil column are needed.

507 5. CONCLUDING REMARKS

508 Dynamic mixed-flow and column laboratory experiments of soil dissolution in 509 aqueous solutions revealed similar behaviour for different type of soils developed on 510 calcareous or loess parent materials (calcaric cambisol, hypereutric cambisol, albeluvisol and 511 luvisol) suggesting similar mechanisms responsible for release of Si (R_{Si}) from the bulk of soil 512 mineral matrix. The R_{Si} of studied soils was 1 to 2 orders of magnitude higher than that of 513 common soil clays, and 1 to 3 orders of magnitude lower than that of plant phytoliths. 514 Moreover, in contrast to clays and biogenic silica, the R_{Si} of whole soils weakly depended on 515 pH at 4 < pH < 8 (decreased by a factor 1.5 to 2 for hypereutric cambisol and calcaric 516 cambisol; independent for luvisol, and increasing 2-fold for albeluvisol). As such, the two 517 dominant 'bulk' pools of Si cannot explain the magnitude and pH-dependence of its release 518 rate from soils. We hypothesize that either amorphous allophanes, imogolite, organo-Fe-Al-Si 519 compounds (poorly known from the view point of dissolution kinetics), or Si desorption from 520 common soil minerals (Fe and Al hydroxides) can be responsible for labile Si pool released from soil into aqueous solution. This pool of reactive Si amounted to 0.04-0.08 mg Si g_{soil}^{-1} 521

which is largely sufficient to provide the Si requirements of common plants in forest soils,and it can be mobilized into aqueous solution within first hours of contact with the fluid.

524 The reactivity of soils measured in this study demonstrates that very small fraction of 525 actual soil present at the watershed (< 0.1-1%) is capable to provide the observed Si concentration in soil porewater and Si export flux from the watershed. Although we studied 526 527 only limited number of soils, developed on loesses and calcareous substrates, we observed 528 rather similar values of Si release rate regardless of the soil type, agricultural use, and solution 529 pH. This may help to explain relatively low range of Si concentrations and fluxes observed in 530 natural watersheds, compared to drastic differences in reactivity of individual silicate minerals 531 or whole mother rocks inferred from laboratory experiments. Therefore, results obtained in 532 the present study contribute to quantifying bulk soil reactivity with respect to Si release rate. 533 We suggest that R_{Si} of whole soil, rather than that of individual soil minerals and amorphous 534 (biogenic) silica, is better suited for being incorporated in existing reactive transport/chemical 535 weathering models. This calls a need for experimental measurements of labile Si in various 536 soils across the world, ideally using flow-through reactors.

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822	Table 1. Soil origin, description,	physical and chem	ical properties. M	ore information	on is

provided in Cornu et al. (2022). The soils are ordered as following: first the soil developed in

824 calcareous rock containing carbonates, then those in which carbonates were dissolved, then

soils developed in loess, with the most evolved at the end (albeluvisol). SOC is Soil Organic

826 Carbon and SSA is Specific Surface Area.

Soil type	Sample	Sampling	SOC,	pH (*)	< 2 µm	$SSA m^2/q$
(WRB, 2006)	I.D.	depth, cm ^(*)	g kg ^{-1 (*)}		g kg ^{-1 (*)}	55A, m /g
Calcaric	701C1	0-20	47	7.9	491	
Cambisol	701F1	0-20	53	6.8	477	
Calcaric	755C1	0-20	23	8.1	514	49.1
Cambisol	755F1	0-10	69	6.9	695	22.8
	755F2	10-20	39	7.7	514	
Hypereutric	BS2C1	0-25	14	8.1	307	17.8
Cambisol	BS2F1	0-10	39	5.9	282	14.2
	BS2F2	10-25	24	6.1	307	
Hypereutric	1166C1	0-25	17	7.3	341	19.2
Cambisol	1166F1	0-5	45	6.9	376	19.2
	1166F2	5-20	25	6.9	371	

Luvisol	340C1	0-25	11	7.0	156	12.6
	340F1	0-10	23	5.1	136	22.8
	340F2	10-25	11	5.0	134	
Luvisol	62C1	0-25	11	8.0	195	8.05
	62F1	0-5	29	4.1	162	6.11
	62F2	5-35	9.6	4.4	152	
Albeluvisol	BS3C1	0-20	9.5	7.1	160	10.5
	BS3F1	0-15	24	5.3	110	13.5
	BS3F2	15-25	12	4.9	108	

829 (*) Cornu et al. (2022)

832 **Table 2.** Si-based dissolution rates of soils determined in mixed-flow reactors. Here and

833 below, bicarbonate is 10 mM NaCl +1 mM NaHCO₃; acetate is 5 mM NaCl+5 mM acetic

acid. The pH values are measured in the outlet solutions, which corresponds to the steady-

835 state conditions of the dissolution process.

Soil tring	Fluid	Duration,	nII	R _{Si} ,	S.D.	R _{Si} ,	S.D.
Son type	Fluid	h	рн	mol/g _{soil} /h	R _{Si}	mol/m ² /d	R _{Si}
Calcaric	MQ	260	7.13	4.6×10^{-8}	1.2×10^{-8}	-	-
cambisol	Bicarbonate	120	7.74	4.5×10^{-8}	3.4×10 ⁻⁹	-	-
701C1	Acetate	132	4.29	1.1×10^{-7}	4.2×10 ⁻⁹	-	-
Calcaric	MQ	260	6.72	2.7×10^{-8}	6.6×10 ⁻⁹	-	-
cambisol	Bicarbonate	120	7.76	3.8×10^{-8}	3.9×10 ⁻⁹	-	-
701F1	Acetate	132	4.2	5.2×10^{-8}	1.8×10^{-9}	-	-
Coloorio	MQ	288	6.41	8.6×10^{-8}	6.5×10 ⁻⁹	1.2×10^{-8}	2.9×10 ⁻⁹
cambisol	Bicarbonate	204	7.84	7.3×10^{-8}	1.4×10^{-9}	3.6×10 ⁻⁸	6.8×10 ⁻⁹
755C1	Acetate	312	4.25	1.2×10^{-7}	1.5×10^{-8}	6.1×10 ⁻⁸	7.4×10 ⁻⁹
75501	MQ	144	6.78	6.3×10 ⁻⁸	3.5×10 ⁻⁹	3.1×10 ⁻⁸	1.7×10 ⁻⁹
Calcaric	MQ	288	6.86	5.3×10^{-8}	3.6×10 ⁻⁹	5.6×10 ⁻⁸	3.8×10 ⁻⁹
cambisol	Bicarbonate	204	7.78	5.9×10^{-8}	5.9×10 ⁻⁹	6.2×10^{-8}	6.2×10 ⁻⁹
755F1	Acetate	312	4.27	1.2×10^{-7}	4.4×10^{-9}	1.3×10 ⁻⁷	4.6×10^{-9}
75511	MQ	504	5.88	8.1×10 ⁻⁸	1.2×10 ⁻⁸	8.5×10 ⁻⁸	1.3×10 ⁻⁸
Hypereutric	MQ	228	6.43	6.5×10^{-8}	3.1×10 ⁻⁹	1.1×10^{-7}	5.3×10 ⁻⁹
cambisol		216	7 78	6 4×10 ⁻⁸	5 6×10 ⁻⁹	7	0
BS2C1	Bicarbonate	210	1.10	0.4/10	5.0/10	1.1×10 ⁻⁷	9.5×10 ⁻⁹
Hypereutric	MQ	228	6.62	7.4×10^{-8}	7.2×10^{-9}	1.2×10^{-7}	1.2×10 ⁻⁸
cambisol	Bicarbonate	288	7.93	7.2×10^{-8}	8.6×10 ⁻⁹	1.2×10^{-7}	1.4×10 ⁻⁸
BS2F1	Acetate	120	4.43	1.1×10 ⁻⁷	1.2×10^{-8}	1.8×10 ⁻⁷	2.1×10^{-8}
	MQ	96	6.41	5.1×10 ⁻⁸	5.2×10 ⁻⁹	8.6×10 ⁻⁸	8.7×10 ⁻⁹
Hypereutric	MQ	288	6.59	6.3×10 ⁻⁸	9.6×10 ⁻⁹	7.9×10 ⁻⁸	1.2×10 ⁻⁸
cambisol	Bicarbonate	204	7.83	6.5×10 ⁻⁸	1.2×10 ⁻⁸	8.2×10 ⁻⁸	1.5×10 ⁻⁸
1166C1	Acetate	312	4.25	9.1×10 ⁻⁸	5.8×10 ⁻⁹	1.1×10 ⁻⁷	7.3×10 ⁻⁹
Hypereutric	MQ	288	6.56	4.9×10^{-8}	4.7×10 ⁻⁹	6.1×10 ⁻⁸	5.8×10 ⁻⁹
cambisol	Bicarbonate	204	7.91	6.7×10 ⁻⁸	4.4×10 ⁻⁹	8.4×10^{-8}	5.5×10 ⁻⁹
1166F1	Acetate	312	4.26	8.7×10^{-8}	2.4×10 ⁻⁹	1.1×10 ⁻⁷	2.9×10^{-9}
	MQ	504	5.74	6.1×10 ⁻⁸	6.7×10 ⁻⁹	7.6×10 ⁻⁸	8.4×10 ⁻⁹
	MQ	288	6.17	3.5×10^{-8}	1.2×10 ⁻⁹	3.7×10 ⁻⁸	1.3×10^{-9}
Luvisol	Bicarbonate	204	7.85	4.7×10^{-8}	2.6×10 ⁻⁹	4.9×10 ⁻⁸	2.8×10 ⁻⁹
340F1	Acetate	24	4.29	5.7×10 ⁻⁸	3.8×10 ⁻⁹	6.1×10 ⁻⁸	3.9×10 ⁻⁹
	MQ	312	5.57	4.4×10 ⁻⁸	3.1×10 ⁻⁹	4.6×10 ⁻⁸	3.2×10 ⁻⁹
	MQ	24	6.27	4.4×10^{-8}	5.2×10 ⁻⁹	8.3×10^{-8}	9.9×10 ⁻⁹
Luvisol	Bicarbonate	12	7.93	6.4×10^{-8}	4.1×10 ⁻⁹	1.2×10^{-7}	7.8×10^{-9}
340C1	Acetate	24	4.26	1.1×10 ⁻⁷	4.2×10 ⁻⁹	2.1×10 ⁻⁷	8.1×10 ⁻⁹
	MQ	312	5.74	4.2×10 ⁻⁸	9.5×10 ⁻⁹	7.9×10 ⁻⁸	1.8×10 ⁻⁹
Luvisol	MQ	228	6.52	6.3×10 ⁻⁸	5.8×10 ⁻⁹	1.9×10 ⁻⁷	1.7×10^{-8}
62C1	Bicarbonate	288	7.84	6.5×10 ⁻⁸	4.5×10 ⁻⁹	1.9×10 ⁻⁷	1.3×10 ⁻⁸
Luvisol	MQ	228	5.97	5.3×10 ⁻⁸	1.9×10^{-8}	2.1×10 ⁻⁷	7.6×10 ⁻⁸

	62F1	Bicarbonate	288	7.89	6.8×10 ⁻⁸	4.6×10 ⁻⁸	2.7×10 ⁻⁷	6.3×10 ⁻⁸
		Acetate	120	4.38	6.2×10^{-8}	2.4×10^{-9}	2.4×10^{-7}	9.2×10 ⁻⁹
		MQ	96	6.16	2.8×10^{-8}	7.3×10 ⁻⁹	1.1×10 ⁻⁷	2.9×10 ⁻⁸
	Albeluvisol	MQ	260	6.03	2.1×10^{-8}	4.8×10 ⁻⁹	2.9×10 ⁻⁹	6.9×10 ⁻¹⁰
	BS3C1 N50g	Bicarbonate	120	7.9	4.5×10^{-8}	5.6×10 ⁻⁹	6.4×10 ⁻⁹	7.9×10^{-10}
	D55C1 N50g	Acetate	132	4.1	2.5×10^{-8}	1.6×10 ⁻⁹	3.6×10 ⁻⁹	2.3×10^{-10}
	Albeluvisol	MQ	260	5.68	2.3×10^{-8}	3.8×10 ⁻⁹	2.9×10 ⁻⁹	4.7×10^{-10}
	BS3F2 N37g	Bicarbonate	120	8.16	3.8×10^{-8}	9.5×10 ⁻⁹	4.8×10^{-9}	1.2×10^{-9}
	D551/2 N57g	Acetate	132	4.11	1.9×10 ⁻⁸	1.5×10^{-8}	2.5×10 ⁻⁹	1.9×10 ⁻⁹
	Albeluvisol	MQ	260	5.51	1.7×10^{-8}	3.4×10 ⁻⁹	1.9×10 ⁻⁹	3.8×10^{-10}
	BS3E1 N/7g	Bicarbonate	120	8.14	3.5×10^{-8}	6.2×10 ⁻⁹	3.9×10 ⁻⁹	6.9×10^{-10}
	<u></u>	Acetate	132	4.06	2.8×10^{-8}	1.4×10 ⁻⁹	3.1×10^{-10}	1.6×10^{-10}
337	Footnote : MQ	is for Milli-Q, d	listilled wa	ater.				
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Table 3. Si release rates (mean \pm s.d.) determined in column-through experiments.

Soil type	Fluid	Duration, h	pH outlet	$R_{\rm Si}$, mol $g_{\rm soil}^{-1}$ d ⁻¹
Calcaric cambisol	Milli-Q	240	6.26	$(3.7\pm2.3)\times10^{-8}$
755 F1 (0.5 g) + 755 F2 (1.5 g)	Acetate	100	4.20*	(6.5±0.79)×10 ⁻⁸
Hypereutric cambisol	Milli-Q	170	5.85	$(1.2\pm0.57)\times10^{-8}$
1166 F1 (1 g) + 1166 F2 (3g)	Acetate	190	4.42	(5.3±1.4)×10 ⁻⁸
Hypereutric cambisol BS2 F1(1 g) + BS2 F2 (3g)	Milli-Q	170	5.07	(1.7±1.4)×10 ⁻⁸
Luvisol	Milli-Q	170	5.26	(6.9±6.8)×10 ⁻⁹
340 F1 (1 g) +	Acetate	190	4.05	$(1.1\pm0.19)\times10^{-8}$
340 F2 (3 g)	Bicarbonate	390	7.95*	$(1.8\pm0.35)\times10^{-9}$
Luvisol	Milli-Q	170	4.58	$(7.7\pm5.5)\times10^{-9}$
62 F1 (1 g) +	Acetate	190	3.97	$(1.1\pm0.18)\times10^{-8}$
62 F2 (3 g)	Bicarbonate	390	8.10*	$(2.6\pm2.2)\times10^{-9}$

* Approximated based on results of mixed-flow reactors.

Table 4. Pools (mean \pm s.d.) of labile, fast-leaching Si determined by integration of Si

900 breakthrough curves in soil column experiments over the first 100 h of reaction.

Soil type	Fluid	Time, h	pН	Pool _{Si} , 1
	Tiulu	Time, ii	outlet	mg kg _{soil} -1
	MO	0-10	6.47	45 ± 8.7
Calcaric cambisol	MQ	10-100	6.11	100 ± 15
755 F1 (0.5 g) + 755 F2 (1.5 g)	Apototo	0-10	4.1*	103 ± 70
	Acetale	10-100	4.2*	83±4.9
	MO	0-10	6.75	48±5.5
Hypereutric cambisol	MQ	10-100	5.46	36±5.8
1166 F1(1 g) + 1166 F2 (3g)	Apototo	0-10	5.02	63±32
	Acetale	10-100	4.06	106±10
Hypereutric cambisol	MO	0-10	5.25	40±7.9
BS2 F1 (1 g) + BS2 F2 (3 g)	MQ	10-100	4.98	31±3.7
	MQ	0-10	5.7	34±13
		10-100	5.15	11 ± 2.1
Luvisol	Acetate	0-10	4.16	3.0 ± 0.7
340 F1 (1 g) + F2 (3 g)		10-100	3.98	21 ± 1.8
	Diagrhonata	0-10	7.85*	4.3±2.4
	Dicarbonate	10-100	7.95*	5.1±0.9
	MO	0-10	4.5	39±15
	MQ	10-100	4.62	19 ± 2.5
Luvisol	Apototo	0-10	3.98	2.4 ± 0.6
62 F1 (1 g) + F2 (3 g)	Acetale	10-100	3.98	15 ± 1.8
	Diagrhoneta	0-10	7.9*	6.2 ± 4.2
	Dicardonate	10-100	8.1*	21±0.9

Table 5. Linear (Pearson) correlation matrix of pools of labile, fast-leaching Si and different
916 Si forms in soils taken from Cornu et al. (2022). Significant correlations at p < 0.01, labelled
917 by asterisk.

Time period, h	Si _{tot} ⁽¹⁾	Si ₀ ⁽²⁾	$\mathrm{Si_d}^{(3)}$	Si _{CaCl2} ⁽⁴⁾	Phytoliths
MQ 0-10 h	-0.72	0.73	0.68	0.94	-0.32
MQ 10-100 h	-0.98*	0.97*	0.93	0.73	-0.40
Acetate 0-10 h	-0.98*	0.99*	0.85	0.92*	-0.60
Acetate 10-100 h	-0.75	0.78	0.55	0.98*	-0.67

919	Footnote:
920	
921	(1) Sitot, total Si content in the soil, including quartz, and all mineral and amorphous forms
922	(2) Si ₀ , poorly crystalline Fe oxides and short-range ordered aluminosilicates such as allophanes and
923	imogolites which were extracted by the oxalate method
924	(3) Si_d , iron oxides extracted by the dithionite-citrate-bicarbonate method
925	(4) Si_{CaCl2} , soluble and bioavailable Si, extracted using the CaCl ₂ method
926	
027	
927	
928	
120	
929	
930	



A. Mixed-flow reactors

B. Flow-through column

Figure 1. Experimental setup of mixed-flow reactors used for measurement of Si release rate
from soils as a function of time and solution pH (A) and flow-through column experiments
used for evaluating water-labile pool of adsorbed Si (B).



Figure 2. Examples of Si release pattern from different soils as a function of time, for

different inlet solutions in the mixed-flow reactor. The inlet solutions were represented Milli-

Q water at pH = 5.6, a mixture of 10 mM NaCl and 1 mM NaHCO₃ at pH = 8, and a mixture of 5 mM NaCl and 5 mM Acetic acid at pH = 4.2. The outlet pH values are listed in Table 2.

For brevity, calcisol is used for hypereutric Cambisol and calcosol is for calcaric Cambisol.



Fig. 3. Si release rate from couple cultivated-forest soils hypereutric cambisol (A), calcaric cambisol (**B**), luvisol (**C**) and albeluvisol (**D**) in mixed-flow reactors plotted as a function of outlet solution pH.



Figure 4. Si release rates for typical soil clay minerals and studied soils as a function of pH at 25°C. Soil clays are represented by smectite (Golubev et al., 2006; Rozalen et al., 2008), kaolinite and illite (Köhler et al., 2003, 2005) and chlorite (Lowson et al., 2005). Black solid line represents dissolution rate of various plant phytoliths (horsetail, larch, fern) taken from Fraysse et al. (2009). Red rectangle marks the range of Si release rate from columns with forest and arable cambisols and luvisols (Ronchi et al., 2015). Grey rectangles denotes the range of Si release rate of allophanes (Ralston et al., 2021).



Figure 5. Examples of silica breakthrough curves in column experiments containing 1 g of surface and 3 g of intermediate horizons of forest soils. The initial (0-100 h) part of the curve was used to quantify the pool of water-labile Si present in the soil. For brevity, calcisol is

used for the hypereutric Cambisol and calcosol denotes the calcaric Cambisol. Three inlet solutions were used in column experiments: Milli-Q water at pH = 5.6, a mixture of 10 mM NaCl and 1 mM NaHCO3 at pH = 8, and a mixture of 5 mM NaCl and 5 mM Acetic acid at pH = 4.2. The outlet pH is listed in Table 3.



Figure 6. Correlations between pools of labile, fast-leaching Si measured in column filtration
experiments in this study with different Si forms in soils reported by Cornu et al. (2022). A:
MQ 10-100 h and Si₀, silica linked to allophane/imogolites in the form of amorphous
coprecipitates with Fe/Al compounds as assessed by Tamm treatment; (B): acetate 0-10 h and
Si₀; C: acetate 10-100 h versus Si_{CaCl2}, soluble bioavailable Si extracted with CaCl₂.