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## Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers

Jean Marçais, Alexandre Gauvain, Thierry Labasque, Benjamin W Abbott, Gilles Pinay, Luc Aquilina, Francois Chabaux, Daniel Viville, Jean-Raynald de Dreuzy

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22 Silicate weathering rates were surprisingly similar among Brittany aquifers, varying from  
23 0.20 to 0.23 mg L<sup>-1</sup> yr<sup>-1</sup> with a coefficient of variation of 7%, except for the aquifer where  
24 significant groundwater abstraction occurred, where we observed a weathering rate of 0.31  
25 mg L<sup>-1</sup> yr<sup>-1</sup>. The silicate weathering rate was lower for the aquifer in the Vosges Mountains  
26 (0.12 mg L<sup>-1</sup> yr<sup>-1</sup>), potentially due to differences in climate and anthropogenic solute loading.  
27 Overall, these optimized silicate weathering rates are consistent with previously published  
28 studies with similar apparent ages range. The consistency in silicate weathering rates suggests  
29 that DSi could be a robust and cheap proxy of mean residence times for recent groundwater  
30 (5-100 years) at the regional scale. This methodology could allow quantification of seasonal  
31 groundwater contributions to streams, estimation of residence times in the unsaturated zone  
32 and improve assessment of aquifer vulnerability to anthropogenic pollution.

33 *Keywords: silicate weathering rates; Groundwater residence time; Groundwater age;*  
34 *Lumped Parameter Model; Atmospheric anthropogenic tracers (CFCs); Shallow aquifer.*

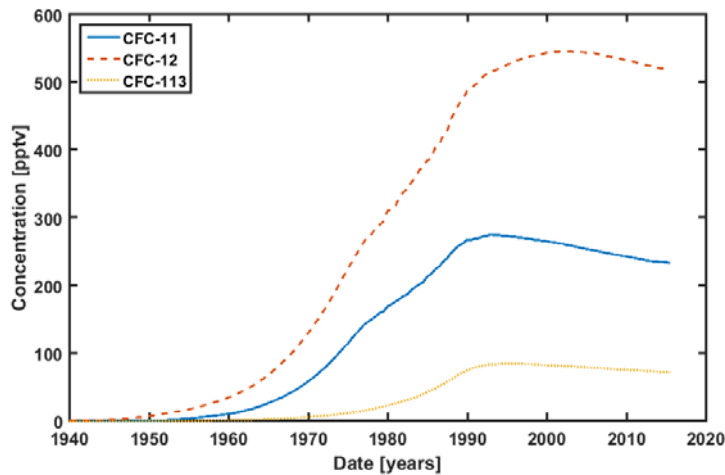
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## 35 **1 Introduction**

36 Human activity has fundamentally altered global nutrient cycles (Galloway et al.,  
37 2008), polluting aquatic ecosystems and threatening human health and water security  
38 (Spalding and Exner, 1993). It is widely held that anthropogenic loading of nitrogen has  
39 exceeded planetary capacities, representing one of the most pressing environmental issues  
40 (Rockstrom et al., 2009; Steffen et al., 2015). International, national, and regional initiatives  
41 have been undertaken in the past several decades to reduce nitrogen loading, though  
42 assessment of efficacy is difficult in complex natural systems with unknown and overlapping  
43 memory effects (Jarvie, 2013; Jenny et al., 2016; Meter and Basu, 2017; Wilcock et al.,  
44 2013). Estimating the recovery time of surface and groundwater ecosystems following  
45 nitrogen pollution is key to quantifying effectiveness of changes in agricultural practices,

46 mitigation methods, and developing realistic timelines for meeting regulatory goals (Abbott et  
47 al., 2018; Bouraoui and Grizzetti, 2011; Jasechko et al., 2017). Recovery time depends largely  
48 on water and solute residence time in the surface and subsurface components of the  
49 catchment. The majority of catchment transit time occurs in the subsurface, where water can  
50 spend months to years in the soil or unsaturated zone (Meter et al., 2016; Sebilo et al., 2013),  
51 and decades to centuries in near-surface aquifers (Bohlke and Denver, 1995; Kolbe et al.,  
52 2016; Singleton et al., 2007; Visser et al., 2013). Because no single tracer can determine the  
53 distribution of groundwater ages across these timescales, multi tracer approaches are  
54 necessary for reliable groundwater dating (Abbott et al., 2016).

55         Several tracers are well suited to determine residence times for timescales relevant to  
56 nutrient pollution, including  $^3\text{H}/^3\text{He}$  and chlorofluorocarbons (CFCs), because the  
57 atmospheric concentration of these gases were altered by human activity coincident with the  
58 great acceleration of nutrient loading in the mid-1900s (Aquilina et al., 2012b; Cook and  
59 Herczeg, 2000; Labasque et al., 2014; Steffen et al., 2015; Visser et al., 2014). However, CFC  
60 methods now lack resolution in the 5-20 years range because their atmospheric concentrations  
61 peaked around 1998 following their prohibition by the Kyoto Protocol (**Figure 1**). This  
62 reversal of atmospheric trends means any measured concentration between 1995 and 2018  
63 corresponds to two dates. Additionally,  $^3\text{H}/^3\text{He}$  and CFC samples are relatively difficult to  
64 collect and costly to analyze, limiting their use to infer residence times of groundwater in  
65 remote environments and much of the developing world. Therefore, there is great interest in  
66 developing new tracers for inferring mean residence time of young groundwater (Morgenstern  
67 et al., 2010; Peters et al., 2014; Tesoriero et al., 2005).



68

69 **Figure 1:** Atmospheric time series of CFC concentrations [pptv] since 1940. The lack of variations since  
70 the 2000s limits their resolution in the last 20 years. Adapted from (Cook and Herczeg, 2000).

71 One promising family of potential groundwater tracers is natural weathering products  
72 such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and dissolved silica (DSi) (Abbott et al., 2016). DSi has been found to be  
73 correlated with apparent age in several site-specific studies (Bohlke and Denver, 1995; Burns  
74 et al., 2003; Clune and Denver, 2012; Denver et al., 2010; Edmunds and Smedley, 2000;  
75 Kenoyer and Bowser, 1992; Kim, 2002; Lindsey et al., 2003; Morgenstern et al., 2015;  
76 Morgenstern et al., 2010; Peters et al., 2014; Rademacher et al., 2001; Stewart et al., 2007;  
77 Tesoriero et al., 2005). However, variability of weathering rates has not been precisely  
78 investigated and DSi has rarely been considered a robust tracer of groundwater age, though it  
79 has been used as a relative indicator of residence time (Beyer et al., 2016; Edmunds and  
80 Smedley, 2000). Two specific challenges to using DSi as a widespread proxy of mean  
81 residence times are: 1. DSi lacks a time-based modeling framework and 2. it is unknown if  
82 silicate weathering rates are stable enough at geologic formation to regional scales to  
83 practically exploit DSi concentration.

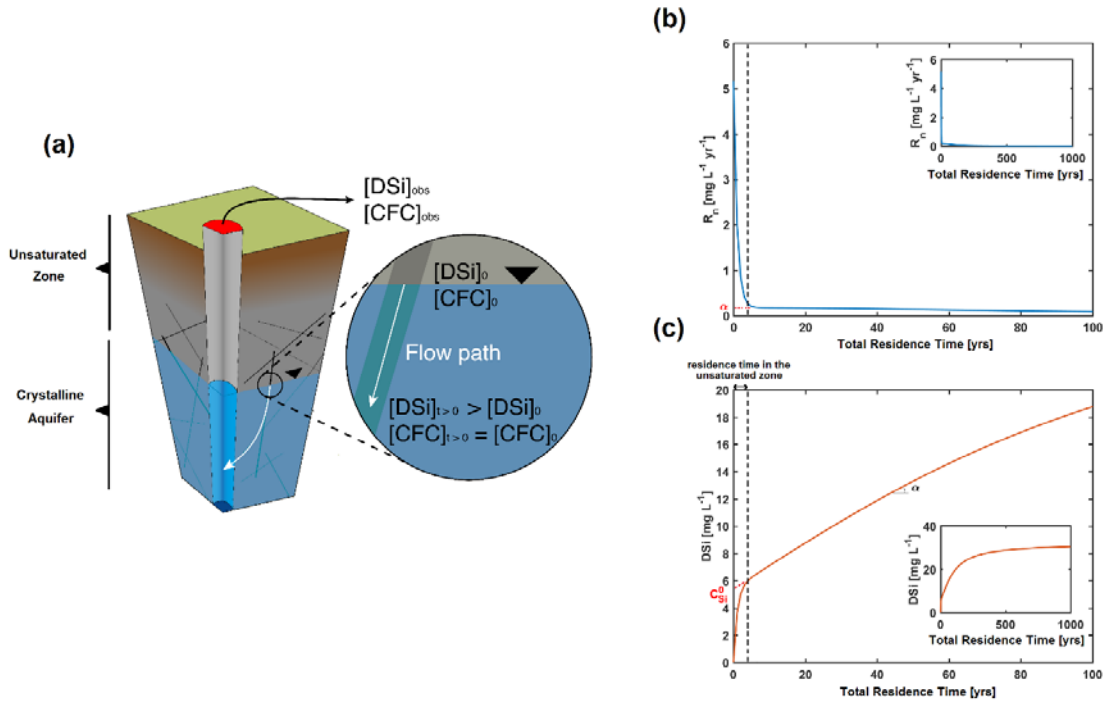
84 In this context, we developed a new approach using groundwater DSi to determine  
85 residence time distributions (RTDs) by calibrating apparent silicate weathering rates with

86 atmospheric groundwater age tracers (CFCs). We were motivated by the following questions:  
87 1. Over what timescales can DSi be used as a tracer of groundwater age? 2. How variable is  
88 the rate of silicate weathering among shallow aquifers, i.e. a few tens of meters deep, with  
89 different lithology? We hypothesized that a simple zero-order kinetic reaction could simulate  
90 weathering rate in shallow aquifers, because hydrolysis would remain transport-limited to  
91 thermodynamically-limited on decadal timescales (detailed in section 2.1). Conversely, a  
92 time-variant weathering rate (i.e. a first order kinetic reaction) would be necessary to account  
93 for mineral equilibrium limitation in aquifers with longer residence times and a broader range  
94 of residence times (Appelo and Postma, 1994; Maher, 2010). We tested these hypotheses by  
95 modeling residence time distributions (RTDs) and weathering dynamics in 5 shallow  
96 crystalline aquifers with contrasting lithology in Brittany and the Vosges Mountains, France.  
97 We used conventional groundwater chemistry and dissolved CFCs from agricultural and  
98 domestic wells to calibrate chemodynamic models for each catchment, using an inverse  
99 Gaussian lumped parameter model to simulate RTDs. We compared our approach with  
100 previous methods and explored potential applications for regional issues of groundwater  
101 quality.

## 102 **2 Approach, catchment description, and geochemical data**

### 103 **2.1 Silicate weathering and DSi concentration**

104 Natural weathering products like DSi are cheap to measure and potentially contain  
105 additional information on residence time distribution compared to atmospheric tracers. Indeed  
106 they are sensitive to the overall residence time in both the unsaturated and saturated zones  
107 (**Figure 2**), whereas atmospheric tracers are only sensitive to the residence time in the  
108 saturated zone (Cook and Herczeg, 2000).



109

110 **Figure 2:** Weathering dynamics justifying our hypothesis of a zero-order kinetic reaction for the  
 111 weathering of silicate minerals in shallow crystalline aquifers. On the time scales considered (5-50 years),  
 112 the weathering rate  $\alpha$  can be considered constant due to transport-limited and thermodynamically-limited  
 113 conditions (Maher, 2010). (a) Conceptual scheme illustrating the evolution of a groundwater flow path  
 114 from the unsaturated zone into the shallow aquifer. (b) Corresponding weathering rate evolution on two  
 115 different timescales. (c) Resulting DSi groundwater concentration evolution along a groundwater flow path.

116 Weathering is a rate-limited, non-equilibrium reaction consisting of physical, chemical,  
 117 and biological processes that occur when mineral surfaces (e.g. bedrock) are exposed to water  
 118 flow (Anderson et al., 2002). Weathering occurs in virtually all terrestrial environments  
 119 including soils, sediments, and subsurface aquifers, and depends partly on the time that  
 120 groundwater has spent in contact with the rock (Maher, 2011). Silicate weathering is the  
 121 predominant weathering process because silicate minerals constitute more than 90% of the  
 122 earth's crust (White, 2008).

123 As water moves through porous or fractured silicate substrate, it dissolves some silica  
 124 by hydrolysis (Maher, 2010). When surface water enters the subsurface, the initial rate of

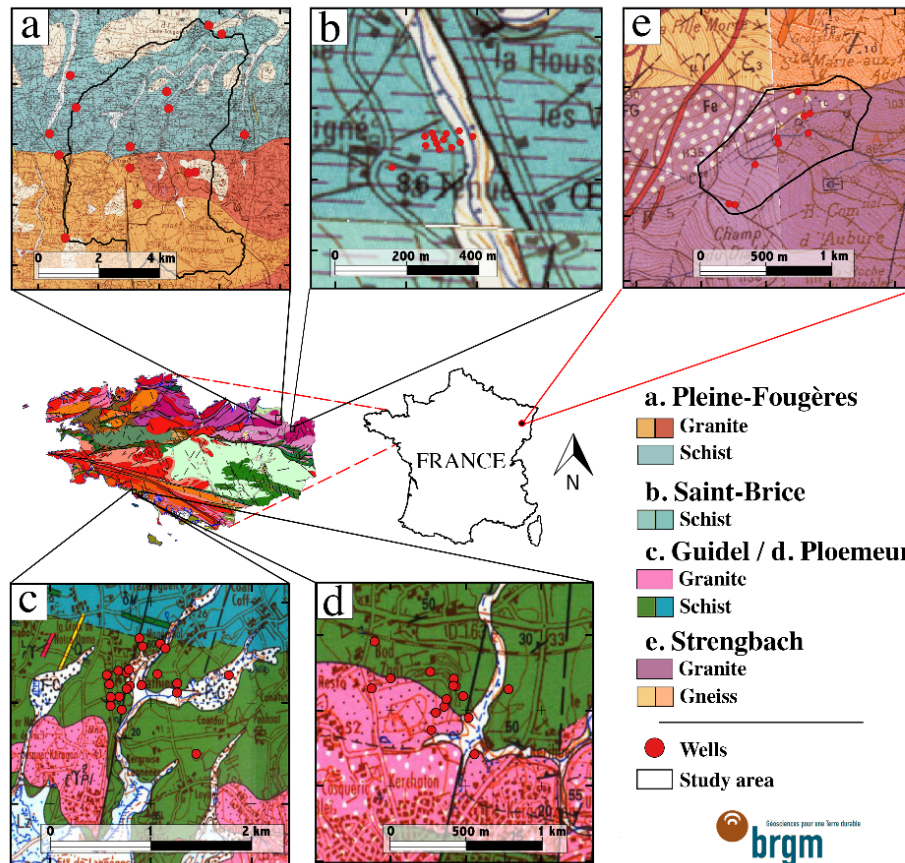
125 silica hydrolysis is determined solely by the contact area between water and rock (*surface-*  
126 *limited weathering*). As water percolates deeper, DSi concentration increases at the rock-  
127 water interface, slowing hydrolysis unless diffusive and advective mixing remove weathering  
128 products from the interface (*transport-limited weathering*). Finally, as DSi concentration in  
129 the whole water mass approaches saturation, second-order equilibrium reactions control  
130 hydrolysis through precipitation of secondary phases (*thermodynamically-limited weathering*)  
131 (Ackerer et al., 2018; Lucas et al., 2017; Maher, 2010). Consequently, hydrologic processes  
132 directly mediate weathering rate, because the speed and routing of water flow control the  
133 transport of solute and the cumulative mineral surface encountered by a volume of water.

134 Differences in weathering rates along and among flow lines can create spatial variations  
135 in DSi concentrations, depending on multiscale dispersive and mixing transport processes  
136 (Gelhar and Axness, 1983). While the signature of detailed water-rock interactions is  
137 progressively erased by mixing processes, the homogenized concentration is more  
138 representative of mean weathering rate. Bulk transport models, including lumped parameter  
139 models, have been developed to analyze the distribution of residence times making up a mean  
140 value on the basis of realistic transport conditions (Green et al., 2014; Haggerty and Gorelick,  
141 1995; Maloszewski and Zuber, 1996). Because these models simulate recharge conditions and  
142 transfer processes through time, they can integrate both atmospheric and lithologic tracers,  
143 providing a flexible framework for inferring transport and weathering information from  
144 multiple proxies of fundamental physical and chemical processes (Abbott et al., 2016;  
145 Marçais et al., 2015). Specifically, lumped parameter models overcome practical limitations  
146 in inferring weathering rates and determining residence times (e.g. determining the mixing  
147 that led to observed CFC concentrations), by explicitly accounting for vertical sample  
148 integration in wells and the diversity of flow paths contributing to that point (Maher and  
149 Druhan, 2014; Marçais et al., 2015)



## 150 2.2 Catchment description

151 We assessed the suitability of DSi as a groundwater age tracer with data from five  
152 catchments. Four of the five study catchments (**Figure 3**) are located in Brittany, France,  
153 where the climate is oceanic and average precipitation ranges from 900 mm yr<sup>-1</sup> in Plœmeur  
154 and Guidel catchments to 960 mm yr<sup>-1</sup> in Pleine Fougères and Saint Brice catchments  
155 (Jiménez-Martínez et al., 2013; Thomas et al., 2016a; Touchard, 1999). Land use in all these  
156 catchments is dominated by agriculture (i.e. 70-90% of arable land used for row crops) and in  
157 one of them, the aquifer is intensively pumped for municipal water supply (Plœmeur,  
158 hereafter the *pumped catchment*; pumping rate = 110 m<sup>3</sup> hr<sup>-1</sup>). The Pleine Fougères, Saint  
159 Brice and Guidel catchments are designated hereafter as *agricultural catchments* 1, 2, and 3,  
160 respectively. The fifth catchment is located in the Vosges Mountain (Strengbach, hereafter the  
161 *mountainous catchment*), in a forested region with elevation ranging from 880 to 1150 m, an  
162 oceanic mountainous climate, and average annual precipitation of 1400 mm yr<sup>-1</sup> (Pierret et al.,  
163 2014; Viville et al., 2012). Though all 5 catchments are underlain by crystalline bedrock  
164 (**Figure 3**), they differ in underlying lithology (granite or schist) and catchment size (from 0.8  
165 to 35 km<sup>2</sup>; **Table 1**). They all have slightly acidic groundwater with pH between 5 and 7  
166 (**Table 1**). Groundwater temperature is more variable among the catchments, ranging from  
167 8°C in the high-elevation mountainous catchment to ~13°C in the lowland Brittany  
168 catchments. The pumped catchment displays the strongest spatial variability of groundwater  
169 temperature, varying between 12 and 17°C due to the pumping activity (**Table 1**). Detailed  
170 site information is provided in the supplementary information and the references are listed in  
171 **Table 1**.



172

173 **Figure 3:** Site locations on the geological map of Brittany (center-left) with detailed site maps of lithology  
 174 and well location for (a) Pleine Fougères, (b) Saint Brice (c) Guidel, and (e) Plœmeur, which is a pumping  
 175 site for drinking water supply. (d) Strengbach is a headwater located in the Vosges Mountains (east part of  
 176 France). Adapted from the Bureau de Recherches Géologiques et Minières (BRGM) data.

### 177 2.3 Geochemical data

178 For each catchment, we analyzed CFC-12, CFC-11, CFC-113, and DSi concentrations  
 179 determined during field campaigns between 2001 and 2015. We only used sampling dates  
 180 where DSi and at least one CFC were simultaneously measured. Because the sampling of DSi  
 181 and CFCs is relatively straightforward (a filtered and acidified water sample for DSi and  
 182 water collected in a stainless-steel vial for CFCs), there were multiple, spatially-distributed  
 183 replicates for each catchment corresponding to different sampling wells or sampling  
 184 campaigns (i.e. 32 replicates on average for each catchment, see **Table 1**). DSi was quantified

185 as  $\text{H}_4\text{SiO}_4$  ( $\text{mg L}^{-1}$ ), from  $0.2\mu\text{m}$  filtered and acidified samples by inductively coupled plasma  
186 mass spectrometry (ICP-MS) at the Geoscience Rennes laboratory, with an uncertainty of  
187  $\pm 2\%$  (Bouhnik-Le Coz et al., 2001; Roques et al., 2014b). CFC concentrations were measured  
188 by purge and trap gas chromatography at the CONDATE EAU laboratory, at the OSUR in the  
189 University of Rennes 1 (France), with a precision of  $\pm 4\%$  for high concentrations and  $\pm 20\%$   
190 for samples near the quantification limit ( $0.1 \text{ pmol L}^{-1}$ ; Labasque et al. (2014); Labasque et al.  
191 (2006)). Dissolved concentrations were converted to atmospheric partial pressures (pptv) with  
192 Henry's law, considering gas solubility and excess air effects (Busenberg and Plummer,  
193 1992). Samples showing obvious contamination with CFCs were excluded from the analysis  
194 (7% of samples were above the maximum atmospheric concentration of CFC).  
195 Contamination, which occurred primarily at the pumped catchment, was likely due to  
196 manufacturing or maintenance activities in the nearby military airport.

<i>Catchment ID</i>	<i>Catchment Name</i>	<i>Area (km<sup>2</sup>)</i>	<i>Lithology</i>	<i>Number of Wells</i>	<i>Number of data (number of data used)</i>	<i>Percentage of polluted data</i>	<i>pH</i>	<i>Water Temperature (°C)</i>	<i>Unsaturation Zone Thickness (m)</i>	<i>Supplementary Information</i>	<i>References</i>
<i>Agricultural catchment 1</i>	<i>Pleine Fougères</i>	<i>35</i>	<i>Granite (50%) and Schist (50%)</i>	<i>18</i>	<i>21(20)</i>	<i>0%</i>	<i>5.2-7.2</i>	<i>11-14</i>	<i>-</i>	<i>Moderate agricultural inputs</i>	<i>(Kolbe et al., 2016)</i>
<i>Agricultural catchment 2</i>	<i>Saint Brice</i>	<i>1</i>	<i>Mainly Schist</i>	<i>11</i>	<i>48(45)</i>	<i>6%</i>	<i>5.3-7.1</i>	<i>12-14.6</i>	<i>2.2-5.1-9.4</i>	<i>Moderate agricultural inputs</i>	<i>(Roques et al., 2014b)</i>
<i>Agricultural catchment 3</i>	<i>Guidel</i>	<i>2.9</i>	<i>Schist</i>	<i>10</i>	<i>18(18)</i>	<i>0%</i>	<i>-</i>	<i>14-14.7</i>	<i>0.5-5.3-18</i>	<i>1 km from the sea - Moderate agricultural inputs</i>	<i>(Bochet, 2017; Bochet et al., under revision)</i>
<i>Pumped catchment</i>	<i>Plœmeur</i>	<i>2.5</i>	<i>Granite and Schist</i>	<i>16</i>	<i>65(58)</i>	<i>11%</i>	<i>5.4-6.5</i>	<i>12-17.3</i>	<i>7-12-30</i>	<i>Pumping site</i>	<i>(Le Borgne et al., 2006; Leray et al., 2012)</i>
<i>Mountainous catchment</i>	<i>Strengbach</i>	<i>0.8</i>	<i>Granite</i>	<i>11</i>	<i>17(17)</i>	<i>0%</i>	<i>5.6-7</i>	<i>7.6-9.3</i>	<i>0-2.5-6</i>	<i>Mountainous headwater (Vosges)</i>	<i>(Chabaux et al., 2017; Viville et al., 2012)</i>

197 **Table 1:** Characteristics of the study sites. The sites display contrast in size, lithology, and geochemical conditions especially regarding water temperature. For the  
198 unsaturated zone thickness, the minimum, average and maximum thickness of the unsaturated zone (m) are reported.

### 199 **3 Modelling residence times and silicate weathering rates**

200 To test our regional uniformity hypothesis, we simultaneously inferred residence times  
201 and silicate weathering rates for all five catchments, using data from the spatially distributed  
202 replicates within each catchment to derive representative weathering rates. We developed a  
203 standardized methodology requiring minimal a priori information to calibrate the lumped  
204 parameter models for the determination of RTDs. CFCs and DSi concentrations were jointly  
205 used to calibrate the lumped parameter models for each replicate (i.e. well), while weathering  
206 rates were optimized for each catchment to minimize the overall mismatch between modeled  
207 and measured concentrations. Following this procedure, silicate weathering rates were derived  
208 from DSi concentrations calibrated with CFC concentrations, which showed broad variability  
209 in mean residence time among sites.

210 Because CFC concentrations depend primarily on the date of groundwater recharge,  
211 while DSi concentration depends on water-rock interactions, these two tracers potentially  
212 contain complementary information about RTDs. In the following sections, we present the  
213 assumptions about weathering and types of RTDs, and then detail the calibration strategy  
214 aiming at determining weathering at the scale of the catchment and RTD properties for each  
215 well.

#### 216 **3.1 Weathering assumptions**

217 Chemical weathering of silicate minerals is the net result of the dissolution of primary  
218 silicate minerals minus the precipitation of secondary mineral formation (Anderson and  
219 Anderson, 2010). To model the effect of residence times on overall observed DSi  
220 concentrations, we considered that precipitation and dissolution rate constants lead to a net  
221 weathering rate  $\alpha$  [ $\text{mg L}^{-1} \text{yr}^{-1}$ ], which corresponds to the enrichment rate of groundwater in  
222 DSi.

223 At the intermediate scale (10s to 100s of meters), this net weathering rate encounters a  
224 rapid transition from surface-limited to transport-limited weathering. During this transition,  
225 weathering rates may differ in the unsaturated zone as minerals differ from the deeper  
226 unaltered zone and water contains lower DSi concentrations, which together favor surface  
227 reaction-limited processes. While we did not estimate unsaturated zones weathering rates, we  
228 did account for differences in DSi concentration at the water table (see next paragraph). Time-  
229 based observations in crystalline formations show that weathering rates do not depend on  
230 residence times for groundwater older than few months to decades, due to transport and  
231 thermodynamic controls, which sustain the weathering (Ackerer et al., 2018; Maher, 2010;  
232 White and Brantley, 2003). Given that the shallow crystalline aquifers investigated in this  
233 study have CFC apparent ages greater than 25 years (Ayraud, 2005; Ayraud et al., 2008;  
234 Kolbe et al., 2016; Leray et al., 2012; Roques et al., 2014a), we assumed that  $\alpha$  stays  
235 constant i.e. that the net weathering follows a zero-order kinetic reaction.

236 The DSi concentration from the dissolution of silicates in the unsaturated zone is  
237 assumed to lead to an initial DSi concentration  $C_{Si}^0$ , which does not depend on the  
238 groundwater residence time  $t$  (i.e. the amount of time water spends in the unsaturated zone  
239 may be unrelated to the subsequent residence time in the aquifer).  $t$  only represents the  
240 residence time in the aquifer because it is inferred from CFC concentrations, which  
241 equilibrate at the water table (**Figure 2a**). Therefore, assuming a constant weathering rate  $\alpha$   
242 and an initial DSi concentration  $C_{Si}^0$  reached at the water table results in a linear expression of  
243 the DSi concentration as a function of the residence time  $t$  [yr]:

$$C_{Si}^{prod}(t) = \begin{cases} \alpha t + C_{Si}^0 & \text{if } t < t_{max} \\ C_{Si}^{max} = \alpha t_{max} + C_{Si}^0 & \text{if } t \geq t_{max} \end{cases}, \quad (1)$$

244 where  $t_{max}$  is the time at which groundwater becomes saturated in DSi (i.e. precipitation or  
 245 removal equals dissolution). Indeed, at larger scale, mineral equilibrium can be reached.  
 246 However, recent hydrogeochemical modeling of weathering in the mountainous catchment  
 247 showed that silica equilibrium is not reached until kilometers of transport, much farther than  
 248 typical flow distance between recharge areas and sampling wells or surface water features  
 249 (Ackerer et al., 2018; Kolbe et al., 2016; Lucas et al., 2017). Additionally, for many  
 250 catchments there is a negligible contribution of groundwater with residence times longer than  
 251 100 years (age at which the groundwater is likely to encounter DSi saturation) as shown by  
 252 the presence of CFCs in the groundwater of these catchments. Therefore,  $C_{Si}^{prod}$  only depends  
 253 on residence time  $t$ , weathering rate  $\alpha$  and initial DSi concentration  $C_{Si}^0$  at the water table.

### 254 3.2 Modeling groundwater mixing

255 Multiple geological, topographical, and hydraulic factors influence RTDs. Distributed  
 256 groundwater flow and transport models were previously developed for the agricultural  
 257 catchment 1 and the pumped catchment, showing that the general shape of the RTDs can be  
 258 well approximated by an inverse Gaussian function in most cases (Kolbe et al., 2016; Marçais  
 259 et al., 2015). Inverse Gaussian distributions have proved especially efficient for providing  
 260 accurate predictions of distribution quantiles and integrated renewal times within the time  
 261 range where information can theoretically be extracted from CFC tracers (i.e. 0-70 years,  
 262 **Figure 1**). Previous studied sites have also shown that the choice of the lumped parameter  
 263 model is not critical as long as it has two parameters and is unimodal (Eberts et al., 2012;  
 264 Kolbe et al., 2016; Marçais et al., 2015). Inverse Gaussian distributions have the additional

265 advantage of being physically grounded as they are the solution of the 1D advection  
 266 dispersion equation:

$$f_{\mu,\sigma}(t) = \frac{1}{\sigma} \sqrt{\frac{\mu^3}{2\pi t^3}} \exp\left(-\frac{\mu(t-\mu)^2}{2\sigma^2 t}\right), \quad (2)$$

267 where  $t$  is the residence time,  $\mu$  is mean time and  $\sigma$  is the standard deviation. The two  
 268 degrees of freedom of an inverse Gaussian distribution are sufficient to adapt to most  
 269 observed hydraulic conditions found in upland sites, which show narrow distributions similar  
 270 to Dirac distributions, and in lowland sites near the surface flow outlet, which express more  
 271 exponential shapes (Haitjema, 1995). We therefore used inverse Gaussian distributions for all  
 272 catchments, though a different lumped parameter model's choice could be easily implemented  
 273 if hydraulic conditions required it (Leray et al., 2016).

274 Inferring RTDs with an inverse Gaussian LPM requires determining two parameters:  
 275 the mean residence time  $\mu$  and the standard deviation  $\sigma$  of the distribution. For a given  
 276 Inverse Gaussian RTD  $f_{(\mu,\sigma)}$ , the concentrations in CFCs can be modeled as:

$$\begin{aligned} C_{CFC-12}^{\text{mod}}(t_s, \mu, \sigma) &= \int_0^{+\infty} C_{CFC-12}(t_s - u) \cdot f_{(\mu,\sigma)}(u) du \\ C_{CFC-11}^{\text{mod}}(t_s, \mu, \sigma) &= \int_0^{+\infty} C_{CFC-11}(t_s - u) \cdot f_{(\mu,\sigma)}(u) du, \\ C_{CFC-113}^{\text{mod}}(t_s, \mu, \sigma) &= \int_0^{+\infty} C_{CFC-113}(t_s - u) \cdot f_{(\mu,\sigma)}(u) du \end{aligned} \quad (3)$$

277 where  $u$  is the residence time,  $t_s$  is the sampling date,  $t_s - u$  is the recharge date (when the  
 278 water reaches the water table) and  $C_{CFC}$  is the corresponding CFC atmospheric time series  
 279 (**Figure 1**). Integrating over all the potential residence times, the product of the RTD  $f_{(\mu,\sigma)}$



280 with the CFC concentration present at the water table at  $t_s - u$  gives the modeled CFC  
 281 concentration. Similarly, the modeled concentration in DSi can be expressed as:

$$C_{Si}^{\text{mod}}(\alpha, C_{Si}^0, \mu, \sigma) = \int_0^{+\infty} C_{Si}^{\text{prod}}(\alpha, C_{Si}^0, u) \cdot f_{(\mu, \sigma)}(u) du, \quad (4)$$

282 where  $C_{Si}^{\text{prod}}$  is the DSi concentration produced during the residence time  $u$  via weathering  
 283 (equation (1)). Equations (3) and (4) give the modeled concentrations of CFCs and DSi,  
 284 which depend on the LPM parameters  $(\mu, \sigma)$ , and on the catchment-based weathering  
 285 parameters  $(\alpha, C_{Si}^0)$ , related to site characteristics.

### 286 3.3 Calibration strategy: inferring conjointly RTDs and silicate weathering rates

287 With  $N$  wells on a given catchment and  $N$  concentrations of CFCs and DSi  
 288  $(C_{CFC-12_k}^{\text{mes}}, C_{CFC-11_k}^{\text{mes}}, C_{CFC-113_k}^{\text{mes}}, C_{Si_k}^{\text{mes}})_{1 \leq k \leq N}$ , the calibration strategy consisted in optimizing  
 289 together (i.e. for the  $N$  datasets) the weathering rate  $\alpha$ , the initial concentration of DSi  $C_{Si}^0$ ,  
 290 and the best inverse Gaussian LPMs  $(\mu_k, \sigma_k)_{1 \leq k \leq N}$  for each of the  $N$  wells. We defined the  
 291 following objective function to optimize the calibration:

$$\begin{aligned}
& \Phi(\alpha, C_{Si}^0, \mu_1, \sigma_1, \dots, \mu_N, \sigma_N) = \\
& \frac{1}{3N} \sum_{k=1}^N \left[ \left| \tilde{C}_{Si-k}^{mes} - \tilde{C}_{Si-k}^{mod}(\alpha, C_{Si}^0, \mu_k, \sigma_k) \right| + \right. \\
& \min \quad \tilde{C}_{CFC-12k}^{mes} - \tilde{C}_{CFC-12k}^{mod}(t_{s_k}, \mu_k, \sigma_k) + \tilde{C}_{CFC-11k}^{mes} - \tilde{C}_{CFC-11k}^{mod}(t_{s_k}, \mu_k, \sigma_k), \\
& \quad \tilde{C}_{CFC-12k}^{mes} - \tilde{C}_{CFC-12k}^{mod}(t_{s_k}, \mu_k, \sigma_k) + \tilde{C}_{CFC-113k}^{mes} - \tilde{C}_{CFC-113k}^{mod}(t_{s_k}, \mu_k, \sigma_k), \\
& \quad \left. \tilde{C}_{CFC-11k}^{mes} - \tilde{C}_{CFC-11k}^{mod}(t_{s_k}, \mu_k, \sigma_k) + \tilde{C}_{CFC-113k}^{mes} - \tilde{C}_{CFC-113k}^{mod}(t_{s_k}, \mu_k, \sigma_k) \right],
\end{aligned} \tag{5}$$

292 where  $\tilde{C}$  are the standardized and centered values of  $C$ . In equation (5), the minimum  
 293 conveys that we only retain the two most coherent CFC concentrations with their respective  
 294 modeled counterparts out of the three CFC concentrations available (Jurgens et al., 2012).

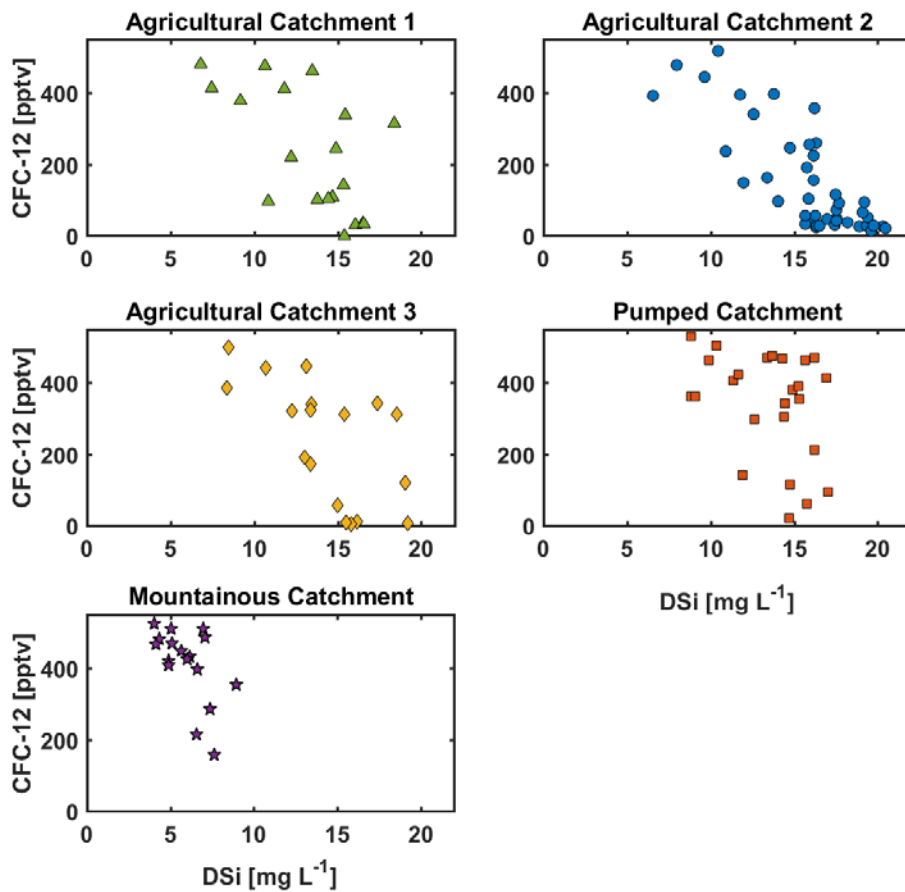
295 Because of some non-convexity of the objective function  $\Phi$ , we use a two-step  
 296 optimization method with an initial calibration of  $(\alpha, C_{Si}^0)$  with the simulated annealing  
 297 Monte-Carlo method in MATLAB (Ingber, 2000), and a second gradient-based Levenberg-  
 298 Marquardt optimization to complete the reduction of the set of parameters. Using this  
 299 methodology, weathering rates were compared among the catchments to test for regional  
 300 differences in weathering rate.

## 301 4 Results

302 We first report observed CFC and DSi concentrations for the different catchments and  
 303 then use the methodology presented in section 3 to derive the catchment-level weathering  
 304 rates and individual well RTDs.

#### 305 4.1 Observed CFC and DSi concentrations

306 The relationship between CFCs and DSi was generally negative, though the strength of  
307 the relationship and range of values varied by catchment (see **Figure 4**). Given the theoretical  
308 relationship between CFCs and DSi, **Figure 5** shows the concentrations of CFC-12 and DSi  
309 that can be reached with Inverse Gaussian RTDs, whatever their mean and standard  
310 deviations in the range of 0-100 years for the two silicate weathering rates, i.e.  
311 ( $\alpha = 0.25 \text{ mg L}^{-1}\text{yr}^{-1}, C_{Si}^0 = 4 \text{ mg L}^{-1}$ ) and ( $\alpha = 0.5 \text{ mg L}^{-1}\text{yr}^{-1}, C_{Si}^0 = 8 \text{ mg L}^{-1}$ ). Each point  
312 represents an Inverse Gaussian RTD with specific parameters. Sampling well data of the  
313 agricultural catchment 1 are shown as green triangles on the same plot for illustrative  
314 purposes and the best RTD associated for each well sampled is represented among the  
315 different Inverse Gaussian RTD by orange circles. The lower weathering scenario  
316 ( $\alpha = 0.25 \text{ mg L}^{-1}\text{yr}^{-1}, C_{Si}^0 = 4 \text{ mg L}^{-1}$ ) explained much of the variability observed in the CFC-12  
317 and DSi concentrations, suggesting that it is closer to the *in situ* rate. The difference between  
318 the two envelopes underlines the high sensitivity of the weathering model and gives some  
319 preliminary illustration of the capacity of extracting meaningful weathering properties.

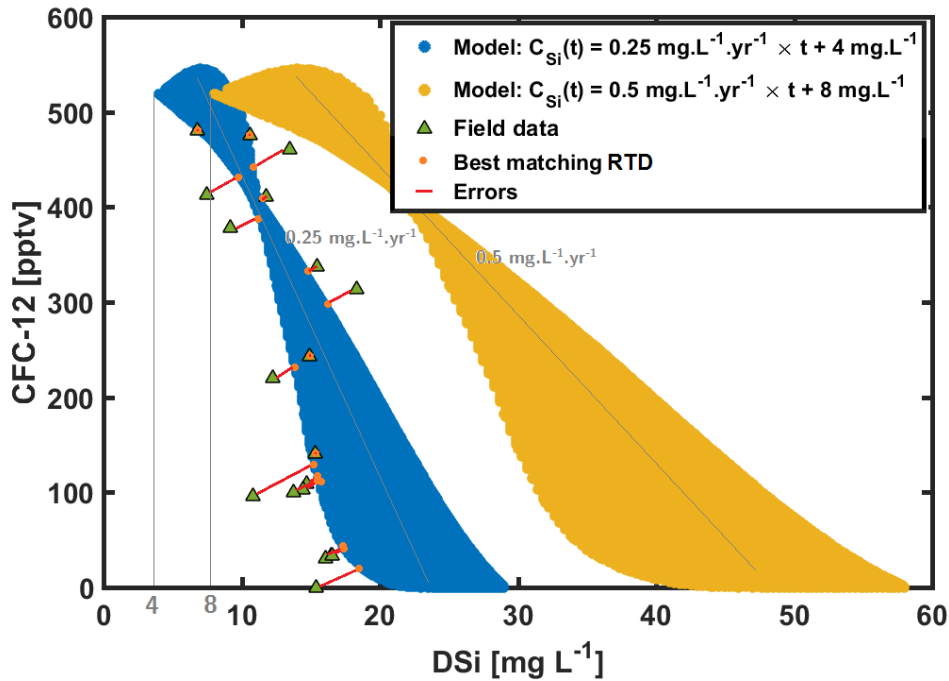


320

321 **Figure 4:** CFC-12 vs DSi concentrations obtained for each of the field sites.

## 322 4.2 Catchment-based optimal weathering rates

323 We applied the same optimization method for each of the 5 catchments.  $\rho$  (the average  
 324 model error) varied significantly among catchments, with relatively small values (below 0.25)  
 325 for most of the catchments, but higher values for the pumped catchment ( $\rho = 1.64$ ; **Table 2**).  
 326 Optimal weathering rates were relatively similar among catchments, especially for the  
 327 agricultural catchments, which ranged from 0.20 to 0.23 mg L<sup>-1</sup>yr<sup>-1</sup> (CV = 7%), demonstrating  
 328 regional consistency among different rock types. The weathering rate was significantly slower  
 329 (0.12 mg L yr<sup>-1</sup>) in the mountainous catchment and significantly faster in the pumped  
 330 catchment (0.31 mg L yr<sup>-1</sup>).



331

332 **Figure 5:** Calibration methodology. For each dataset representative of one site (Field data), the equation of  
 333 weathering (1) is optimized by minimizing the sum of the square errors between the well data and their best  
 334 matching Inverse Gaussian RTD in the RTD model ensemble. Two models ensemble are represented: the  
 335 blue one with  $(\alpha, C_{Si}^0) = (0.25 \text{ mg L}^{-1} \text{ yr}^{-1}, 4 \text{ mg L}^{-1})$  and the yellow one with  $(\alpha, C_{Si}^0) = (0.5 \text{ mg L}^{-1} \text{ yr}^{-1},$   
 336  $8 \text{ mg L}^{-1})$ . Notice how  $C_{Si}^0$  controls the horizontal position of the RTDs models in the (CFC, DSi) plot,  
 337 especially for the young fraction of the RTDs (high CFC-12, low DSi) while  $\alpha$  controls the overall DSi  
 338 spreading of the models ensemble, especially for the old fraction of the RTDs (low CFC-12, high DSi).

339 Optimal initial DSi concentrations ( $C_{Si}^0$ ) displayed some variability with a coefficient of  
 340 variation of 19% among catchments. On the extremes, the mountainous catchment showed an  
 341 initial DSi of  $2.9 \text{ mg L}^{-1}$  while the pumped catchment had an initial concentration of  
 342  $5.0 \text{ mg L}^{-1}$ , likely due to differences in weathering in the unsaturated zone.

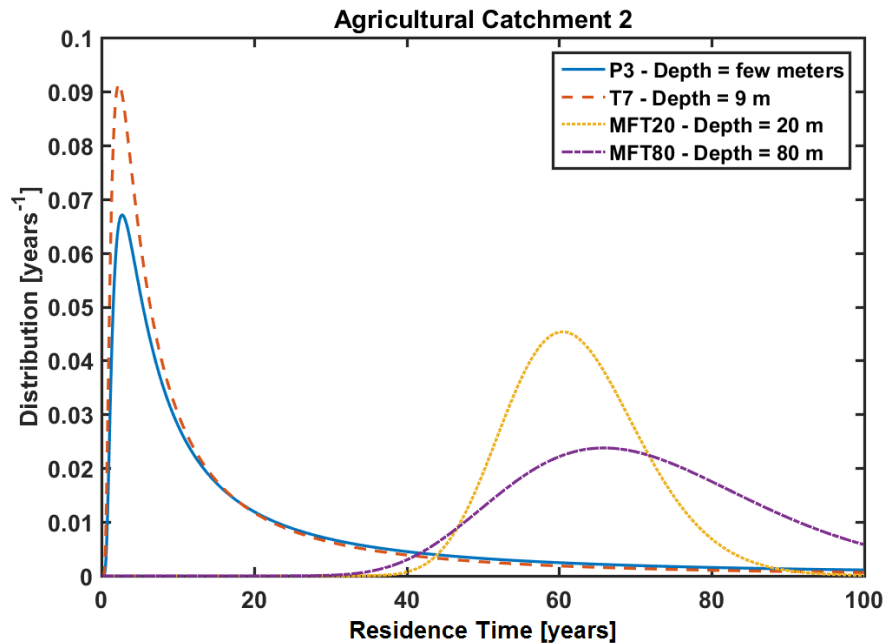
Catchment	$\rho$ [-]	$\alpha$ [ $\text{mg L}^{-1} \text{ yr}^{-1}$ ]	$C_{Si}^0$ [ $\text{mg L}^{-1}$ ]	mean ( $\mu$ ) [yr]	mean ( $\sigma$ ) [yr]
Agricultural catchment 1	0.12	0.20	4.0	52	39

<i>Agricultural catchment 2</i>	<i>0.26</i>	<i>0.22</i>	<i>3.8</i>	<i>60</i>	<i>32</i>
<i>Agricultural catchment 3</i>	<i>0.23</i>	<i>0.23</i>	<i>4.3</i>	<i>52</i>	<i>49</i>
<i>Pumped catchment</i>	<i>1.64</i>	<i>0.31</i>	<i>5.0</i>	<i>40</i>	<i>53</i>
<i>Mountainous catchment</i>	<i>0.19</i>	<i>0.12</i>	<i>2.9</i>	<i>30</i>	<i>59</i>

343 **Table 2:** Results obtained from the calibration.  $\rho$  is the residual (see equation (1)).  $\alpha$  is the weathering  
344 rate in  $\text{mg L}^{-1} \text{yr}^{-1}$ ,  $C_{\text{Si}}^0$ , the initial DSi concentration in  $\text{mg L}^{-1}$ . The two last columns present some  
345 statistics about the parameters of the inverse Gaussian distributions optimized for each well: the average of  
346 the mean residence time  $\mu$  in years and the average of the standard deviation  $\sigma$  in years of the residence  
347 time distributions for each catchment.

### 348 4.3 Models of RTDs

349 The largest differences between well-level RTDs occurred in the agricultural catchment  
350 2 (**Figure 6**). The wells intersecting deep productive fractures had high DSi concentration and  
351 low CFC concentrations (**Figure 4**) and displayed broad RTDs between 40 and 100 years  
352 (**Table 2** and yellow and purple curves in **Figure 6**). The low CFC concentrations  
353 corresponded with the modeled RTDs, which indicated limited modern water (less than 15 to  
354 20 years' old). High DSi concentration requires much longer timescales and can be modeled  
355 as well by the contribution of residence times above 40 years. The water residence time  
356 distributions of the shallow wells (blue and red curves of **Figure 6**) showed significantly  
357 younger water due to the lack of the old water contributions coming from deeper fractures  
358 (**Figure 6**).



359

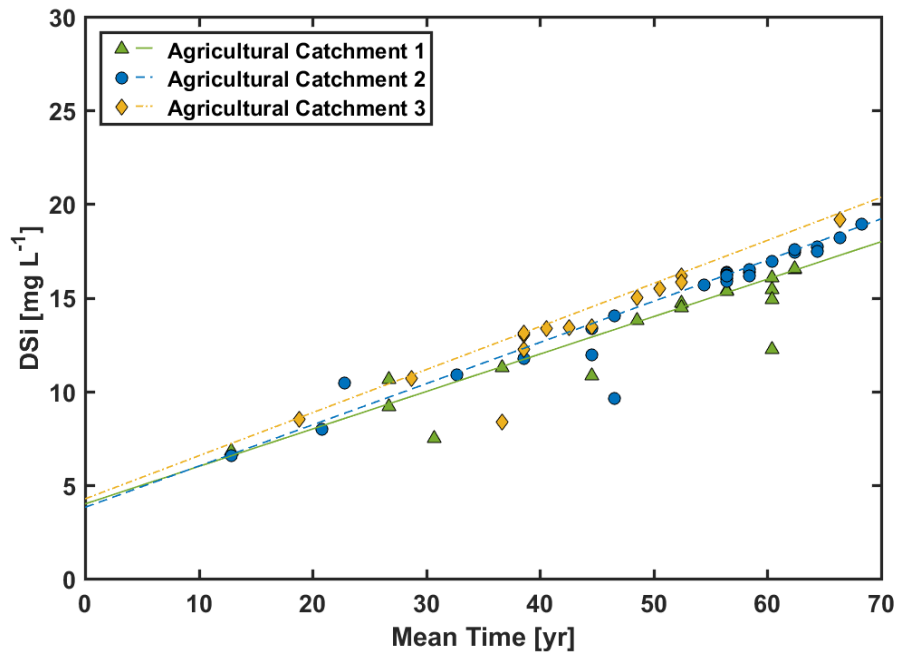
360 **Figure 6:** Illustration of the calibrated Inverse Gaussian RTD obtained on the agricultural catchment 2  
 361 (Saint Brice). The wells lying in the shallowest part of the aquifers have small residence times and  
 362 exponential shapes. The wells lying in the deepest part of the aquifer display some skewed distributions.

363 To get an idea of the type of RTDs obtained for the other catchments, we also compared  
 364 some statistics of the RTDs between sites, obtained with the optimization reported in **Table 2**.  
 365 All catchments have RTDs with mean residence times, which range on average between 30  
 366 years for the mountainous catchment and 60 years for the agricultural catchment 2.

#### 367 4.4 Relations between DSi and mean residence times

368 A byproduct of the calibration of the inverse Gaussian lumped parameter model for the  
 369 DSi and CFC concentrations was the relation between the modeled mean residence times and  
 370 the observed DSi concentrations here shown for the three agricultural catchments located in  
 371 Brittany (**Figure 7**). For each catchment, the relation appeared to be linear, reinforcing the  
 372 consistency between the observed and modeled concentrations, and providing support for the  
 373 assumptions of the modeling approach. More specifically, the direct proportionality of the  
 374 DSi concentration to the mean residence time validated weathering assumptions modeled by a

375 zero-order kinetic reaction (equation (1)). The linear relations were also similar among  
 376 catchments with coefficients of variation of respectively 7% and 6%, for the different  
 377 weathering rates and the initial DSi concentration of the agricultural catchments.

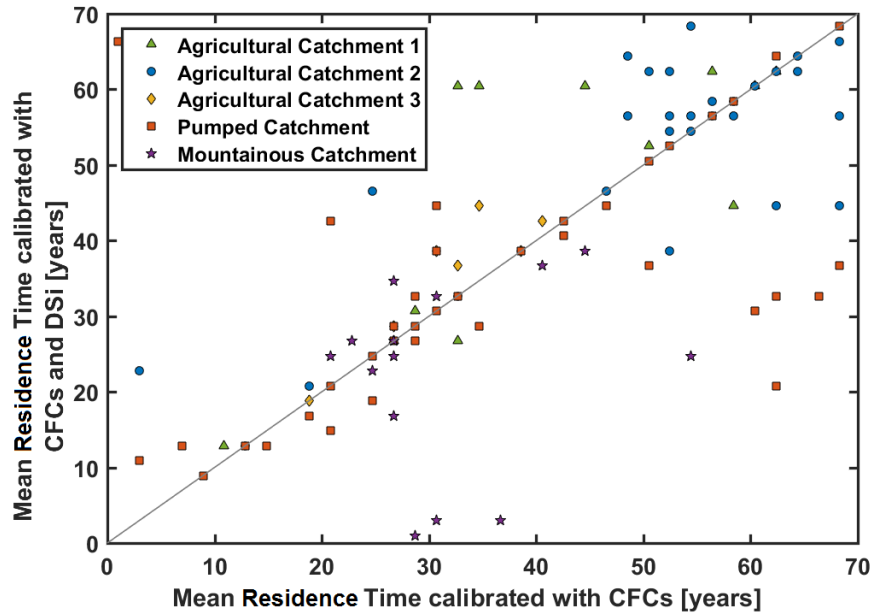


378

379 **Figure 7:** Measured DSi concentration versus the optimized mean residence time of the inverse Gaussian  
 380 lumped distribution for three of the Brittany sites. Straight lines represent the optimized weathering law for  
 381 each of the sites. Note that it fits the measurements. Considering a constant weathering rate allows direct  
 382 interpretation of DSi apparent ages into mean residence times.

383 We compared these modeled mean residence times obtained with the CFC and DSi  
 384 concentrations with the mean residence times calibrated only with the CFC concentrations  
 385 (**Figure 8**). These CFC-only mean residence times were obtained using equation (1) without  
 386 considering DSi concentrations. For each of the wells in the different catchments, the mean  
 387 residence times obtained were quite consistent, especially for mean residence times ranging  
 388 between 0 and 50 years. For such a time range, a linear regression gives  $\mu_{DSi-CFCs} =$   
 389  $1.03 \mu_{CFCs}$  with a  $R^2$  of 0.36.





390

391 **Figure 8:** Comparison between the mean residence time obtained with CFCs and DSi concentrations with  
392 those obtained only with the CFC concentrations.

## 393 5 Discussion

394 While DSi has been used as a site-specific indicator of groundwater residence time  
395 (Burns et al., 2003; Kenoyer and Bowser, 1992; Morgenstern et al., 2010; Peters et al., 2014),  
396 it was unknown how consistent silica weathering rates were, and consequently if DSi could be  
397 a useful tracer at regional scales. In this study, we evaluated the use of DSi for groundwater  
398 dating at four catchments in Brittany and one catchment in the Vosges Mountains. The data  
399 and our simulations supported the hypothesis that silica weathering can be described by a  
400 zero-order kinetic reaction at the catchment scale, and we calibrated silicate weathering laws  
401 using CFC atmospheric tracers. We found that DSi provided complementary information to  
402 CFC atmospheric tracers on RTDs. The relative stability of weathering rates among the  
403 Brittany agricultural catchments validates the use of DSi as a regional groundwater age proxy.  
404 We discuss below how these weathering rates may be modified by climatic context (from the  
405 oceanic conditions of Brittany to the mountainous climate of the Vosges) and by external

406 factors, e.g. groundwater abstraction. Finally, we discuss the use of DSi for evaluating  
407 residence times in unsaturated zones and compare these optimized silicate weathering rates to  
408 weathering rates estimated in previous studies.

### 409 **5.1 Practical use of DSi as a proxy of groundwater residence time**

410 DSi concentration appears to be a highly complementary tracer to atmospheric tracers  
411 such as CFCs. For example, at the agricultural catchment 2 (**Figure 6**), the comparison of  
412 wells of different depths (shallow wells for P3 and T7, and deeper wells for MFT 20 and  
413 MFT80) revealed that DSi concentration can infer the RTD even when CFCs are not  
414 discriminating because they are below their detection limit for older ages (> 70 years) or  
415 during the flat portion of their atmospheric trend (i.e. the last 0-20 years). These time ranges  
416 where CFCs are less informative are further exacerbated by the widening of the concentration  
417 area reachable by the inverse Gaussian function towards lower and higher CFC-12  
418 concentration (**Figure 5**). For such CFC range (for example, for CFC-12 between 450 and  
419 550 pptv and between 0 and 50 pptv), DSi is particularly useful to better characterize RTD.  
420 The comparison between the modeled mean residence times and those calibrated only with  
421 CFCs (**Figure 8**) also displayed an increased consistency for the time range between 0 and 50  
422 years. For mean residence times above 50 years, DSi appears to give complementary  
423 information to mean residence times from CFCs as depicted by the increased variability of  
424 mean residence times around the identity line  $y = x$ .

425 The bulk linear relation for weathering rate (equation (1)) is also of interest for dating  
426 purposes as DSi concentrations can be seen as a direct proxy of the mean residence time  
427 (**Figure 7**), which is not the case for other tracers such as CFCs (**Figure 1**) (Leray et al., 2012;  
428 Marçais et al., 2015; Suckow, 2014). While this result has been obtained with a specific  
429 Lumped Parameter Model (inverse Gaussian), it is generally applicable for a broad range of

430 distributions as it relies on the zero-order weathering assumption that leads to a linear  
431 dependence of the DSi concentration on residence times (equation (1)).

432 Even if the small residuals obtained in **Table 2** indicate that the inverse Gaussian model  
433 may be appropriate for RTDs, other types of distributions, like the Gamma distribution, can  
434 be tested to assess the sensitivity of the LPM choice to the RTD-related prediction. For the  
435 agricultural catchment 1 and the pumped catchment, shapes of the Inverse Gaussian LPM as  
436 well as the statistics obtained regarding the optimized RTDs (**Table 2**) are consistent with  
437 results obtained synthetically from calibrated 3D flow and transport models developed for  
438 these aquifers (Kolbe et al., 2016; Leray et al., 2012).

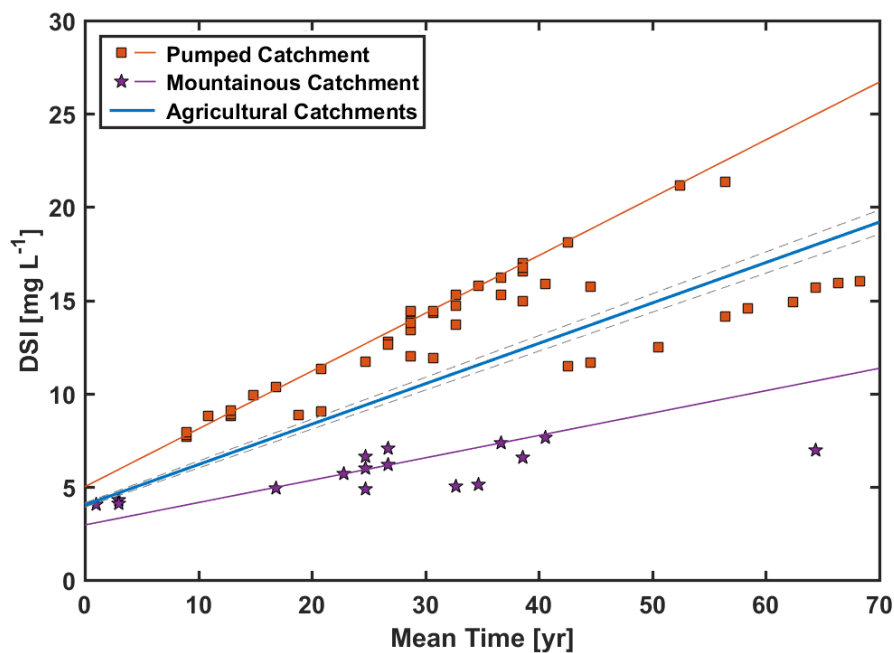
439 The 5 to 100 years' time range of the RTDs observed here is the most favorable case for  
440 using DSi for groundwater dating since it leads to thermodynamic-limitation conditions which  
441 sustains chemical weathering (Maher, 2010). Even though weathering rates  $\alpha$  might be quite  
442 variable between different crystalline rock types, the fluid-rock contact time controls the  
443 evolution of DSi concentrations for residence times ranging from years to decades (5-100  
444 years) where dissolution is the dominant process. On the contrary, attainment of the mineral  
445 equilibrium restricts the use of DSi for estimating longer residence times (>300 years) when  
446 dissolution is balanced by re-precipitation (Edmunds and Smedley, 2000).

## 447 **5.2 Stability of silica weathering rates at the regional scale**

### 448 *5.2.1 DSi as a robust regional groundwater age proxy*

449 Our results indicate that DSi can be used as groundwater age tracing tool in relatively  
450 diverse geologic contexts, as indicated by the consistency of the weathering rates for the  
451 different Brittany catchments (**Figure 7**). This homogeneity suggests that only a few mineral  
452 phases are responsible for silica production in the studied residence-time range; typically  
453 phyllosilicates, plagioclase, and accessory minerals such as apatite are the major sources of

454 silica (Aubert et al., 2001). Applying a uniform weathering rate ( $0.22 \text{ mg L}^{-1} \text{ yr}^{-1}$ ) and initial  
 455 DSi concentration ( $4.0 \text{ mg L}^{-1}$ ) can provide a first order estimate of mean residence time, as  
 456 displayed by the blue curve presented in **Figure 9** compared to the weathering rates of each of  
 457 the Brittany catchments displayed in **Figure 7**. The relatively small error associated with  
 458 catchment specific differences justifies the possible use of DSi as a regional groundwater  
 459 dating tracer, as long as a weathering law can be applied based on similar catchments or land  
 460 lithologies. If more complete modeling is available, the choice between weathering laws can  
 461 be bypassed by directly solving the mass balance of the geochemical water content (Burns et  
 462 al., 2003).



463

464 **Figure 9:** DSi concentrations versus the optimized mean residence time of the inverse Gaussian displayed  
 465 for each wells for the mountainous and the pumped catchment. Straight lines represent the optimized  
 466 weathering law for each of the sites. Note that it fits the measurements. Considering a constant weathering  
 467 rate enables to indistinctly consider Si apparent ages and mean residence times.

468 Silicates are ubiquitous in most geological matrices, including crystalline and  
 469 sedimentary rocks (Iler, 1979). There is some evidence for using DSi as a groundwater age

470 proxy in other rock types (e.g. sedimentary rocks coming from glacial deposits, see section  
471 5.4) (Becker, 2013; Kenoyer and Bowser, 1992). DSi concentration is widely measured and  
472 accessible through public observatories and databases (Abbott et al., 2018; De Dreuzy et al.,  
473 2006; Thomas et al., 2016b). While previous studies have shown dependency of weathering  
474 rates on lithology and climate (White and Blum, 1995; White et al., 1999; White et al., 2001),  
475 DSi might be considered a “contextual tracer”, allowing at least local and potentially regional  
476 groundwater dating (Beyer et al., 2016).

477 A major advantage of DSi is that it persists in open surface waters (e.g. lakes and  
478 streams), whereas other tracers of intermediate transit times such as  $^3\text{H}/\text{He}$  and CFCs quickly  
479 equilibrate with the atmosphere. Additionally, because artificial sources are few and  
480 background concentration is usually high, DSi is robust to contamination, unlike CFCs, which  
481 cannot be in contact with the atmosphere during sampling nor with any plastic surfaces  
482 (Labasque et al., 2014). However, uptake of DSi by some vegetation and diatoms could  
483 potentially limit the use of DSi in some environments especially during the growing season  
484 (beginning of summer) (Delvaux et al., 2013; Pfister et al., 2017). This uptake is more likely  
485 in large rivers systems where DSi spend enough time to be effectively captured by diatoms  
486 whereas it is less prone to occur in headwaters systems with much smaller stream residence  
487 times (Hughes et al., 2013). To track this potential additional process into account, diatom  
488 uptake could be modeled (Thamatrakoln and Hildebrand, 2008) and/or isotopic DSi ratios  
489 could be investigated to link in stream DSi concentration to mean transit time (Delvaux et al.,  
490 2013).

### 491 5.2.2 *Comparison between the agricultural catchments and the mountainous catchment*

492 Weathering rates were relatively constant within a given regional geological and climatic  
493 context (e.g. for the three catchments in Brittany), but they were significantly different from

494 the mountainous catchment (Vosges Mountains). Differences in lithology could control  
495 overall weathering rates, but this was not supported by the observed homogeneity of the  
496 weathering rate across different lithologies (section 5.2.1). Acidity could not either explain  
497 this variability, as pH was comparable for all the catchments (**Table 1**). The lower rates in the  
498 mountainous catchment may be due to a difference in climatic conditions (i.e. temperature  
499 and rainfall) between Brittany and the Vosges Mountain (**Table 1**). The ~3 factor difference  
500 between DSi in the Vosges and Brittany could be explained by the combined effect of the  
501 groundwater temperature difference (~6°C) and precipitation difference (~1.5-fold). Indeed,  
502 temperature affects weathering rates by one order of magnitude from 0 to 25°C (White and  
503 Blum, 1995; White et al., 1999). This increase is further emphasized by increasing recharge  
504 fluxes, which is related to rainfall conditions. Another effect which could explain the  
505 difference for the mountainous catchment is lack of anthropogenic pressure related to  
506 agriculture. Brittany is a region of intensive agriculture characterized by high nitrogen loads,  
507 which induce soil acidification. High weathering rates have been observed related to fertilized  
508 additions (Aquilina et al., 2012a) which may also partially explain the Vosges-Brittany  
509 difference. Anyway, climatic and anthropogenic influences are not exclusive and may be  
510 combined to explain the high weathering rate difference.

### 511 5.2.3 *Effect of groundwater abstraction on the weathering rate*

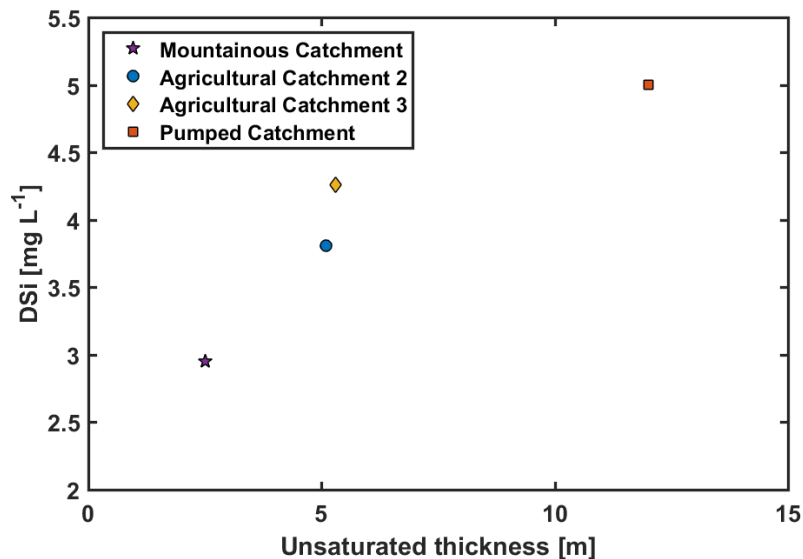
512 The weathering law for heavily-pumped catchment in Plœmeur (orange line, **Figure 9**)  
513 displayed a substantially higher weathering rate ( $0.31 \text{ mg L}^{-1} \text{ yr}^{-1}$ ) compared to the average  
514 Brittany weathering rate ( $0.22 \text{ mg L}^{-1} \text{ yr}^{-1}$ ). This might be due to the presence of CFC  
515 contamination leading to artificially enriched CFC concentrations compared to their actual  
516 residence times. The pumped catchment is indeed especially vulnerable to CFC  
517 contaminations (**Table 1**). However, long-term monitoring of CFC and SF<sub>6</sub> and <sup>3</sup>H/<sup>3</sup>He  
518 measurements in this site makes the contamination hypothesis unlikely (Tarits et al., 2006).

519 The difference is more likely explained by the facts that: *i*) high and long-term pumping has  
520 mobilized older waters (>100 years), which increase DSi concentrations without substantially  
521 altering CFC concentrations (only dilution effect) (**Figure 4**); *ii*) pumping leads to a renewal  
522 of groundwater flow paths with more reactive surfaces, leading to an increase of the reactive  
523 surface/groundwater ratio.

### 524 **5.3 Use of DSi for inferring residence times in the unsaturated zone**

525 We hypothesized that the differences in initial DSi concentration are due to residence  
526 time in the unsaturated zone, suggesting that DSi concentration at the groundwater table  
527 surface (or modeled intercepts) could be used to infer residence times in the unsaturated zone.  
528 Indeed the variability in  $C_{Si}^0$  observed in **Table 2** is correlated with the average unsaturated  
529 zone thickness (**Table 1**), a major, though not exclusive, control on the time spent in the  
530 unsaturated zone (**Figure 10**). The high  $C_{Si}^0$  for the pumped catchment ( $5.0 \text{ mg L}^{-1}$ ) could be  
531 due to pumping-induced drawdown of the water table, which significantly increases the  
532 unsaturated zone thickness. Likewise, the mountainous catchment has a much shallower water  
533 table depth, which might be related to the low initial DSi concentration ( $2.9 \text{ mg L}^{-1}$ ). DSi  
534 could therefore be a tracer of the full residence time in both unsaturated and saturated zones.  
535 Yet, unless weathering rates in the unsaturated zone can be constrained, DSi estimates would  
536 remain qualitative. Through tracing experiments, Legout et al. (2007) estimated the residence  
537 time in the mobile-compartment of the unsaturated zone of the Kerrien catchment (South  
538 Brittany) as  $2\text{-}3 \text{ m y}^{-1}$ , which induces weathering rates about 4 times higher than in the  
539 saturated zone. However, the ratio mobile/immobile water is unknown but may represent a  
540 large fraction of groundwater with long residence-time that may contribute to high DSi.  
541 Because the unsaturated zone, including the base of the soil profile, is often the site of  
542 elevated rates of biogeochemical activity (e.g. nitrogen retention and removal) (Legout et al.,

543 2005) or storage, constraining the residence time of water and solutes in this zone would  
 544 allow better estimation of catchment and regional-scale resilience to nutrient loading and  
 545 overall ecological functioning (Abbott et al., 2016; Meter et al., 2016; Pinay et al., 2015).



546

547 **Figure 10:** Initial DSi concentrations versus the average unsaturated zone thickness. The average  
 548 unsaturated zone thickness of the agricultural catchment 1 was not available.

#### 549 5.4 Comparison of weathering rates to previously estimated weathering rates

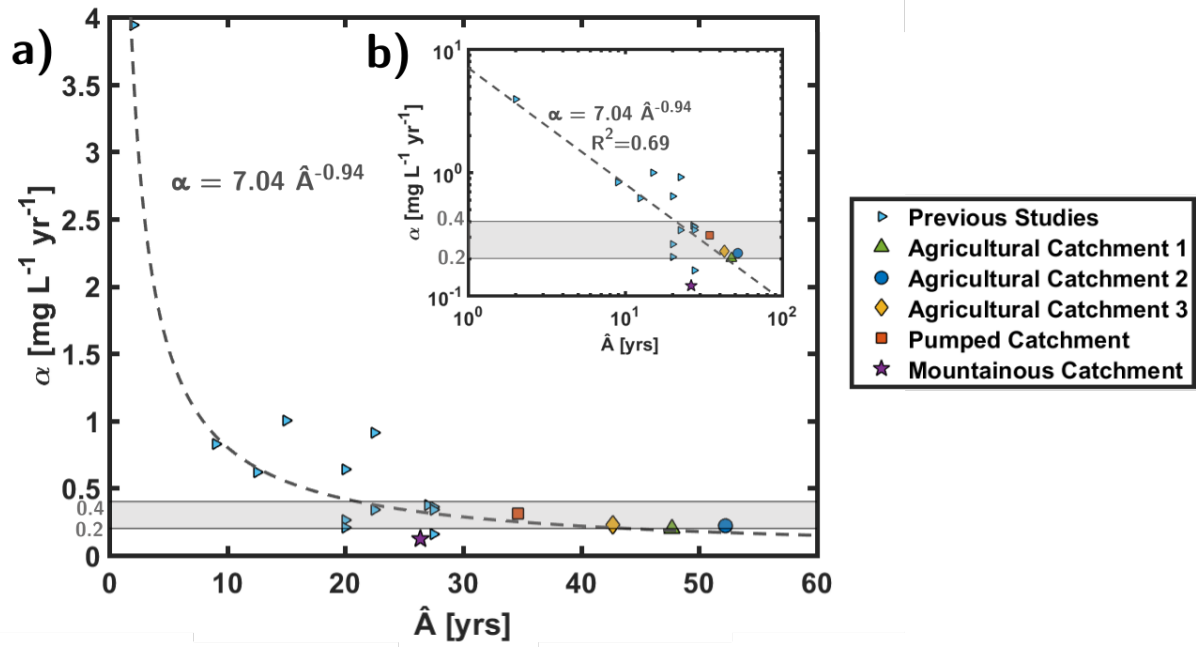
550 We compared the weathering rates obtained in this study with previously published  
 551 studies (**Table 3**). The catchments considered in these studies have crystalline or sedimentary  
 552 bedrocks derived from the erosion of crystalline formations. Apparent weathering rates have  
 553 been estimated by different methods, either by implementing the geochemical evolution of  
 554 groundwater through advanced reactive transport modeling (Burns et al., 2003; Rademacher  
 555 et al., 2001) or by directly comparing DSi concentrations with apparent ages derived from  
 556 atmospheric tracer data (Bohlke and Denver, 1995; Clune and Denver, 2012; Denver et al.,  
 557 2010). Our methodology is intermediary as it combines lumped residence time distributions  
 558 with apparent weathering rates and inlet concentrations (atmospheric chronicles for CFCs and  
 559 initial concentration  $C_{Si}^0$  for DSi).



560           Except for the data reported in Kenoyer and Bowser (1992), which consists of young  
561 groundwater (0-4 yrs), all DSi weathering rates referred in Table 3 are within one order of  
562 magnitude (0.1 to 1 mg L<sup>-1</sup> yr<sup>-1</sup>). For catchments with apparent ages between 10 and 50 years,  
563 weathering rates are clustered between 0.2 and 0.4 mg L<sup>-1</sup> yr<sup>-1</sup> (Figure 11), which is consistent  
564 with weathering rates estimated in this study.

565           The initial decrease of weathering rates with the typical apparent ages might suggest a  
566 power law dependence of weathering rates on groundwater age (Figure 11). However, for  
567 older apparent ages, the weathering rates might also stabilize around 20 years (Figure 11,  
568 insert) suggesting a transition from transport-limited to thermodynamically-limited conditions  
569 consistent with what has been observed for feldspar minerals (Maher, 2010) with a slightly  
570 older transition time (20 years here instead of 10 years). It will require more studies on this  
571 residence time range (0-100 yrs) to decide between these two competing hypotheses (power  
572 law dependence versus stabilization) and precisely locate the transition time (Ackerer et al.,  
573 2018). This could be investigated by systematically combining weathering studies with  
574 groundwater age tracer analysis in a diversity of environmental observatories. If predictable  
575 rates are not found, the use of a constant weathering rate (equation (1)) could be refined by  
576 considering a first order kinetic reaction, although it would require the inference of an  
577 additional parameter to describe weathering.

578



579

580 Figure 11: Silicate weathering rates  $\alpha$  against the typical apparent age range  $\hat{A}$  from which they have been  
 581 obtained, in this study and in previous studies (insert: log-log representation, p-value of  $2 \cdot 10^{-5}$  obtained for  
 582 the fit).

Catchment	$\alpha$ [mg L <sup>-1</sup> yr <sup>-1</sup> ]	Geological Context	Apparent Age range	Complementary information	References
Chesterville Branch	0.34	Permeable sand and gravel units of the fluvial Pensauken Formation and the marine glauconitic Aquia Formation.	5 – 40 yrs	Part of Locust Grove Catchment	(Bohlke and Denver, 1995)
Morgan Creek Drainage	0.37	Permeable sand and gravel units of the fluvial Pensauken Formation and the marine glauconitic Aquia Formation.	4 – 50 yrs	Part of Locust Grove Catchment	(Bohlke and Denver, 1995)
Panola Mountain Research Watershed	0.62	Panola Granite (granodiorite composition), a biotite–oligoclase– quartz–microcline granite of Mississippian to Pennsylvanian age.	0 – 25 yrs	Mainly Riparian Saprolite Aquifer	(Burns et al., 2003)
Bucks Branch Watershed	0.91	Sediments of the Beaverdam Formation.	15 – 30 yrs	mainly fluvial and estuarine deposits of sand, gravel, silt, and clays	(Clune and Denver, 2012)
Fairmount catchment	0.26	Permeable quartz sand and gravel of the Beaverdam Formation and underlying sandy strata of the Bethany Formation.	5 – 35 yrs	well-drained settings with relatively deep water tables and thick sandy aquifers	(Denver et al., 2010)
Locust Grove catchment	0.16	Permeable quartz sand and gravel of the Pensauken Formation underlain by highly weathered glauconitic sands of the Aquia Formation.	5 – 50 yrs	well-drained settings with relatively deep water tables and thick sandy aquifers	(Denver et al., 2010)
Lizzie Catchment	0.36	Several Pleistocene-age terrace deposits that are underlain by a confining unit on the top of the Yorktown Formation.	5 – 50 yrs	predominantly poorly drained settings with shallow water tables	(Denver et al., 2010)
Willards Catchment	0.83	The lowermost unit of the system is the Beaverdam Sand, which is overlain by a 3 to 8 m thick layer of clay, silt, peat, and sand of the Omar Formation.	0 – 18 yrs	predominantly poorly drained settings with shallow water tables	(Denver et al., 2010)
Polecat Creek Watershed	1.0	Piedmont crystalline coastal plain sediments and alluvium. Presence of Saprolite.	0 – 30 yrs	Bedrock garnet-biotite gneiss	(Lindsey et al., 2003)
Crystal Lake, Vilas County (Wisconsin)	3.94	50 m of glacial sediment which overlies Precambrian bedrock.	0 – 4 yrs	Glacial sediments were eroded from Precambrian bedrock lithologies	(Kenoyer and Bowser, 1992)
Sagehen Springs (CA).	0.17 – 1.11	Extensive glacial till deposits derived from a combination of andesite and granodiorite basement rocks. The granodiorite consists primarily of plagioclase (40%), quartz (30%), hornblende (20%), and biotite (10%), and the andesite consists primarily of plagioclase (45%) with varying amounts of hornblende (5–25%) and augite (1–25%) and a small amount of glassy groundmass.	0 – 40 yrs	Range of weathering rate determined for each spring, <b>only for plagioclase mineral.</b>	(Rademacher et al., 2001)
Sagehen Springs (CA).	0.06 - 0.35		0 – 40 yrs	Range of weathering rate determined for each spring, <b>only for hornblende mineral.</b>	(Rademacher et al., 2001)
Lizzie Catchment	0.34	Several Pleistocene-age terrace deposits that are underlain by a confining unit on the top of the Yorktown Formation.	5 – 50 yrs	Unconfined aquifer.	(Tesoriero et al., 2005)

584 **Table 3:** Published weathering rates in different catchments obtained either directly or by fitting DSi concentrations against apparent ages. The typical age range  
585 gives the spread of the water age data obtained from the different sampled wells.

## 586 **6 Conclusion**

587 We investigated the relationship between DSi and groundwater age tracers (CFCs) in five  
588 different crystalline catchments, including lowland, mountainous, and actively pumped  
589 catchments. For each catchment, we quantified the weathering rate and the RTDs at multiple  
590 wells using inverse Gaussian lumped parameter models calibrated with geochemical data.  
591 Overall, the DSi was strongly related to the exposure time between rocks and recently  
592 recharged groundwater (i.e. between 5 to 100 years). We found that DSi was highly  
593 complementary to CFCs, allowing better quantification of RTDs, including in the unsaturated  
594 zone and for water masses younger and older than the now rapidly closing CFC use's  
595 window. The consistency of DSi weathering rates in three Brittany catchments suggests that  
596 DSi may be a robust and cheap groundwater age proxy at regional scales for catchments with  
597 comparable geology and climate. We interpreted DSi accumulation differences in the Brittany  
598 pumped site and the mountainous region, as a consequence of temperature differences and  
599 alterations of flow from groundwater abstraction respectively. If the temperature sensitivity of  
600 weathering can be constrained, this tracer could allow widespread determination of water  
601 transit time at the catchment scale for the unsaturated zone, aquifer, and surface waters.

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