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Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers

Jean Marçais^{†1,2}, Alexandre Gauvain², Thierry Labasque², Benjamin W. Abbott³, Gilles Pinay⁴, Luc Aquilina², François Chabaux⁵, Daniel Viville⁵, Jean-Raynald de Dreuzy²

¹ Agroparistech, 75005 Paris, France

² OSUR, Géosciences Rennes, CNRS, Université de Rennes 1, 35042 Rennes Cedex, France

³ Brigham Young University, Provo, UT, United States

⁴ RiverLy-Irstea, Lyon, 5 rue de la Doua, 69616 Villeurbanne cedex, France

⁵ Laboratoire d'Hydrologie et de Géochimie de Strasbourg (LHyGeS), CNRS, Université de Strasbourg, 67084 Strasbourg Cedex, France

Abstract

Estimating intermediate water residence times (a few years to a century) in shallow aquifers is critical to quantifying groundwater vulnerability to nutrient loading and estimating realistic recovery timelines. While intermediate groundwater residence times are currently determined with atmospheric tracers such as chlorofluorocarbons (CFCs), these analyses are costly and would benefit from other tracer approaches to compensate for the decreasing resolution of CFC methods in the 5-20 years range. In this context, we developed a framework to assess the capacity of dissolved silica (DSi) to inform residence times in shallow aquifers. We calibrated silicate weathering rates with CFCs from multiple wells in five crystalline aquifers in Brittany and in the Vosges Mountains (France). DSi and CFCs were complementary in determining apparent weathering reactions and residence time distributions (RTDs) in shallow aquifers.

[†] Corresponding author: jean.marcais@univ-rennes1.fr

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

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

1 Introduction

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

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

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

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

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

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

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

2 Approach, catchment description, and geochemical data

2.1 Silicate weathering and DSi concentration

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

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

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

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

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

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

2.2 Catchment description

We assessed the suitability of DSi as a groundwater age tracer with data from five catchments. Four of the five study catchments (**Figure 3**) are located in Brittany, France, where the climate is oceanic and average precipitation ranges from 900 mm yr⁻¹ in Plœmeur and Guidel catchments to 960 mm yr⁻¹ in Pleine Fougères and Saint Brice catchments (Jiménez-Martínez et al., 2013; Thomas et al., 2016a; Touchard, 1999). Land use in all these catchments is dominated by agriculture (i.e. 70-90% of arable land used for row crops) and in one of them, the aquifer is intensively pumped for municipal water supply (Plœmeur, hereafter the *pumped catchment*; pumping rate = 110 m³ hr⁻¹). The Pleine Fougères, Saint Brice and Guidel catchments are designated hereafter as *agricultural catchments* 1, 2, and 3, respectively. The fifth catchment is located in the Vosges Mountain (Strengbach, hereafter the *mountainous catchment*), in a forested region with elevation ranging from 880 to 1150 m, an oceanic mountainous climate, and average annual precipitation of 1400 mm yr⁻¹ (Pierret et al., 2014; Viville et al., 2012). Though all 5 catchments are underlain by crystalline bedrock (**Figure 3**), they differ in underlying lithology (granite or schist) and catchment size (from 0.8 to 35 km²; **Table 1**). They all have slightly acidic groundwater with pH between 5 and 7 (**Table 1**). Groundwater temperature is more variable among the catchments, ranging from 8°C in the high-elevation mountainous catchment to ~13°C in the lowland Brittany catchments. The pumped catchment displays the strongest spatial variability of groundwater temperature, varying between 12 and 17°C due to the pumping activity (**Table 1**). Detailed site information is provided in the supplementary information and the references are listed in **Table 1**.

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

2.3 Geochemical data

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

185 as H_4SiO_4 (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 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 (km²)</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>Unsaturated 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.

3 Modelling residence times and silicate weathering rates

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

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

3.1 Weathering assumptions

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

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

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

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

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

3.2 Modeling groundwater mixing

Multiple geological, topographical, and hydraulic factors influence RTDs. Distributed groundwater flow and transport models were previously developed for the agricultural catchment 1 and the pumped catchment, showing that the general shape of the RTDs can be well approximated by an inverse Gaussian function in most cases (Kolbe et al., 2016; Marçais et al., 2015). Inverse Gaussian distributions have proved especially efficient for providing accurate predictions of distribution quantiles and integrated renewal times within the time range where information can theoretically be extracted from CFC tracers (i.e. 0-70 years, **Figure 1**). Previous studied sites have also shown that the choice of the lumped parameter model is not critical as long as it has two parameters and is unimodal (Eberts et al., 2012; 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, μ is mean time and σ 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 μ and the standard deviation σ of the distribution. For a given
 276 Inverse Gaussian RTD $f_{(\mu,\sigma)}$, the concentrations in CFCs can be modeled as:

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

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 $\mathcal{C}_{CFC}$ is the corresponding CFC atmospheric time series
 279 (**Figure 1**). Integrating over all the potential residence times, the product of the RTD $f_{(\mu,\sigma)}$

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

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

where C_{Si}^{prod} is the DSi concentration produced during the residence time u via weathering (equation (1)). Equations (3) and (4) give the modeled concentrations of CFCs and DSi, which depend on the LPM parameters (μ, σ) , and on the catchment-based weathering parameters (α, C_{Si}^0) , related to site characteristics.

3.3 Calibration strategy: inferring conjointly RTDs and silicate weathering rates

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

$$\Phi(\alpha, C_{Si}^0, \mu_1, \sigma_1, \dots, \mu_N, \sigma_N) =$$

$$\frac{1}{3N} \sum_{k=1}^N \left[\left| \tilde{C}_{Si-k}^{mes} - \tilde{C}_{Si-k}^{mod}(\alpha, C_{Si}^0, \mu_k, \sigma_k) \right| + \right. \quad (5)$$

$$\min \quad \tilde{C}_{CFC-12k}^{mes} - \tilde{C}_{CFC-12k}^{mod}(t_{s_k}, \mu_k, \sigma_k) + \tilde{C}_{CFC-11k}^{mes} - \tilde{C}_{CFC-11k}^{mod}(t_{s_k}, \mu_k, \sigma_k),$$

$$\tilde{C}_{CFC-12k}^{mes} - \tilde{C}_{CFC-12k}^{mod}(t_{s_k}, \mu_k, \sigma_k) + \tilde{C}_{CFC-113k}^{mes} - \tilde{C}_{CFC-113k}^{mod}(t_{s_k}, \mu_k, \sigma_k),$$

$$\tilde{C}_{CFC-11k}^{mes} - \tilde{C}_{CFC-11k}^{mod}(t_{s_k}, \mu_k, \sigma_k) + \tilde{C}_{CFC-113k}^{mes} - \tilde{C}_{CFC-113k}^{mod}(t_{s_k}, \mu_k, \sigma_k) \quad ,$$

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 Φ , we use a two-step
 296 optimization method with an initial calibration of (α, 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.

4.1 Observed CFC and DSi concentrations

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

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

4.2 Catchment-based optimal weathering rates

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

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

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

Catchment	ρ [-]	α [$\text{mg L}^{-1} \text{ yr}^{-1}$]	C_{Si}^0 [mg L^{-1}]	mean (μ) [yr]	mean (σ) [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>

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

4.3 Models of RTDs

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

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

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

4.4 Relations between DSi and mean residence times

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

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

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

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

Figure 8: Comparison between the mean residence time obtained with CFCs and DSI concentrations with those obtained only with the CFC concentrations.

5 Discussion

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

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

5.1 Practical use of DSi as a proxy of groundwater residence time

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

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

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

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

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

5.2 Stability of silica weathering rates at the regional scale

5.2.1 DSi as a robust regional groundwater age proxy

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

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

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

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

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

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

5.2.2 Comparison between the agricultural catchments and the mountainous catchment

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

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

5.2.3 Effect of groundwater abstraction on the weathering rate

The weathering law for heavily-pumped catchment in Plœmeur (orange line, **Figure 9**) displayed a substantially higher weathering rate ($0.31 \text{ mg L}^{-1} \text{ yr}^{-1}$) compared to the average Brittany weathering rate ($0.22 \text{ mg L}^{-1} \text{ yr}^{-1}$). This might be due to the presence of CFC contamination leading to artificially enriched CFC concentrations compared to their actual residence times. The pumped catchment is indeed especially vulnerable to CFC contaminations (**Table 1**). However, long-term monitoring of CFC and SF_6 and $^3\text{H}/^3\text{He}$ measurements in this site makes the contamination hypothesis unlikely (Tarits et al., 2006).

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

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

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

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

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

5.4 Comparison of weathering rates to previously estimated weathering rates

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

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

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

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580 Figure 11: Silicate weathering rates α 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	α [mg L ⁻¹ yr ⁻¹]	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, only for plagioclase mineral.	(Rademacher et al., 2001)
Sagehen Springs (CA).	0.06 - 0.35		0 – 40 yrs	Range of weathering rate determined for each spring, only for hornblende mineral.	(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.

6 Conclusion

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

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