

Young runoff fractions control streamwater age and solute concentration dynamics

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Abstract

We introduce a new representation of coupled solute and water age dynamics at the catchment scale, which shows how the contributions of young runoff waters can be directly referenced to observed water quality patterns. The methodology stems from recent trends in hydrologic transport that acknowledge the dynamic nature of streamflow age and explores the use of water age fractions as an alternative to the mean age. The approach uses a travel time-based transport model to compute the fractions of streamflow that are younger than some thresholds (e.g., younger than a few weeks) and compares them to observed solute concentration patterns. The method is here validated with data from the Hubbard Brook Experimental Forest during spring 2008, where we show that the presence of water younger than roughly 2 weeks, tracked using a hydrologic transport model and deuterium measurements, mimics the variation in dissolved silicon concentrations. Our approach suggests that an age–discharge relationship can be coupled to classic concentration–discharge relationship, to identify the links between transport timescales and solute concentration. Our results highlight that the younger streamflow components can be crucial for determining water quality variations and for characterizing the dominant hydrologic transport dynamics.

KEYWORDS

hysteresis, solute concentration, water age, water quality, weathering

1 | INTRODUCTION

Temporal variation in stream water chemistry is the complex by-product of the ensemble of hydrological and biogeochemical transformations that occur within the contributing catchment and along its drainage network. The amount of time solutes (and water) are retained within a catchment before being released to the stream, and then being collected as water samples at an established catchment outlet, represents a fundamental control on stream water chemical composition and variation. Hence, water age and solute transport are intimately linked and are often studied in a coupled manner (e.g., Beyer, Jackson, Daughney, Morgenstern, & Norton, 2016; Bishop, Seibert, Köhler, & Laudon, 2004; Böhlke & Denver, 1995; Hrachowitz *et al.*, 2016; Peters, Burns, & Aulenbach, 2014; Rinaldo & Marani, 1987). Although water age itself cannot be tracked or measured, the analysis of tracers represents the

primary means to infer water age or travel times empirically. For conservative solutes, the chemical composition of streamflow can be seen as a weighted average of the chemical composition of previous (either recent or old) precipitation inputs—whose relative importance is expressed by the distribution of ages that are represented in the sample. For reactive solutes (i.e., for solutes that are involved in biogeochemical transformations along hydrologic flow paths), the age of water is a critical measure of the time available for biogeochemical processes that determine element release and transport.

The link between stream water age and solute concentration becomes particularly relevant for solutes that are controlled primarily by kinetically driven processes, such as the dissolution of silicon (Si) in many watershed systems (e.g., Hornberger, Scanlon, & Raffensperger, 2001). Indeed, when atmospheric contributions are small, the primary input of dissolved Si to the watershed subsurface

is through chemical weathering at the water–mineral interface. Mineral weathering can be seen as a sequence of complex geochemical reactions driven by properties of fluid flow, such as the contact time between the circulating water and mineral surfaces, and fluid chemistry such as acidity and redox potential (e.g., Stumm & Morgan, 1996). Accordingly, the greater the water age, the closer the solute concentration will be to an equilibrium concentration with the near-mineral, surface region (Maher & Chamberlain, 2014).

2 | THE YOUNGER COMPONENT OF STREAMFLOW

Although stream water solute concentration is influenced by the relative abundance of all the water ages, from the youngest (e.g., hours) to the oldest (years), it is worth noting that not all of the catchment water storage contributes equally to streamflow generation, with the younger fractions of storage typically contributing the majority of flow (Harman, 2015). The terminology *young* refers in this context to the younger water (i.e., days to few months) mainly stored in the upper soil horizons, as opposed to the older water characteristically stored in perennial groundwater bodies.

A typical shape of an age distribution is illustrated in Figure 1, which represents the ages of water included in a stream sample. The younger component encompasses a relatively narrow range of ages, where each individual age (together with its solute content) can make an important contribution to the sample. Conversely, the older water component is composed of a very large range of ages (and associated chemical contributions), where each one has little individual impact on the sample composition. The ability to quantify the age distribution of streamflow through concentration measurements strongly depends on the characteristic timescales of the solute input to the system. Water components significantly older than the input timescale will include a large, undifferentiated mixture of all past input compositions, resulting in a quite undetermined old water portion of the age distribution. Different solutes are hence suitable to quantify the presence of different ages. For conservative atmospheric tracers such as water stable isotopes, the

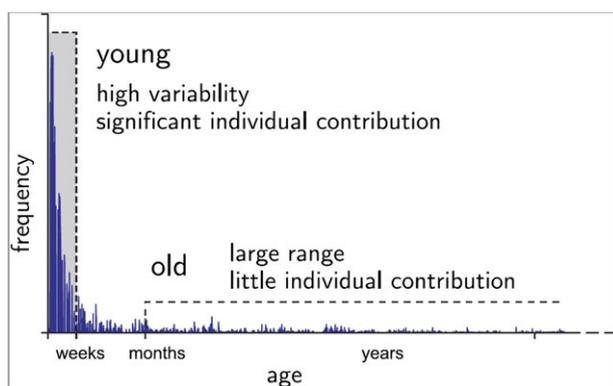


FIGURE 1 Illustrative example of a hypothetical streamflow age distribution. The young component comprises a small range of ages, which all make an important contribution to the sample. The old component, instead, is made of a very large number of little contributions. The right tail of the distribution is typically undetermined, as it is difficult to estimate the presence of very old waters

critical input timescale is the periodicity of precipitation concentration, which typically has a seasonal cycle of 1 year (plus some event-based variations). In this case, water older than 4–5 years can hardly be quantified and other atmospheric tracers such as tritium become more favourable (see Stewart, Morgenstern, McDonnell, & Pfister, 2012). For geogenic solutes, the critical input timescale follows the chemical reactions that release elements into the mobile phase (often expressed through the nondimensional Damköhler number; Oldham, Farrow, & Peiffer, 2013). In this case, all waters older than the time required to reach chemical equilibrium (Maher & Chamberlain, 2014) have the same concentration and can hardly be distinguished from each other.

The difficult quantification of the older water ages has recently led to the use of new aspects of the age distribution other than the mean age, to focus on the younger—and more informative—part of the age distribution. For example, the use of percentiles (such as the median age) to describe properties of the age distribution is more desirable, as they are less impacted by the uncertainty of the old components (e.g., Soulsby et al., 2015). Another example is represented by the “young water fraction” (Kirchner, 2016a, 2016b), which expresses the fraction of discharge that is younger than some threshold. In typical catchment settings, it was shown that the fraction of water younger than approximately 2–3 months is critical in determining the tracer cycle damping from precipitation to streamflow, and this approach was further used to quantify the contribution of young water (i.e., less than 2–3 months in this case) to runoff from catchments worldwide (Jasechko, Kirchner, Welker, & McDonnell, 2016).

3 | YOUNG WATER RELEASE DURING A HIGH-FLOW PERIOD

To highlight the dynamics of young water in streams, we can evaluate the evolution of different young water fractions during the hydrologic response by introducing an age–discharge plot, similar to the concentration–discharge plots often used in hydrochemistry (e.g., Evans & Davies, 1998). To illustrate the potential of the approach, we use hydrochemical data gathered at the Hubbard Brook Experimental Forest (HBEF), New Hampshire (USA), and the modelling framework presented by Benettin et al. (2015). The modelling framework was built on a coupled hydrological and chemical model based on travel times and calibrated on a 4-year deuterium dataset. In the model, the calibrated age structure was then used to drive catchment-scale, first-order linear kinetics to simulate a 14-year record of stream water dissolved Si and sodium concentrations. For this analysis, a 2-month period characterized by high flows (intense snowmelt and precipitation during the spring of 2008) was used. We set three different age thresholds and tracked the release of water younger than those thresholds (i.e., we tracked three different young water fractions). The three thresholds are 3 days, which is representative of “event” water; 13 days, which is the value of the calibrated kinetic constant for Si and is thus an estimate of the characteristic timescale of weathering processes; and 60 days, which is significantly longer than the kinetic constant. We show in Figure 2 the evolution of the different water fractions during the considered period. The event water (age < 3 days) has a rather erratic behaviour as it depends on the availability of new water

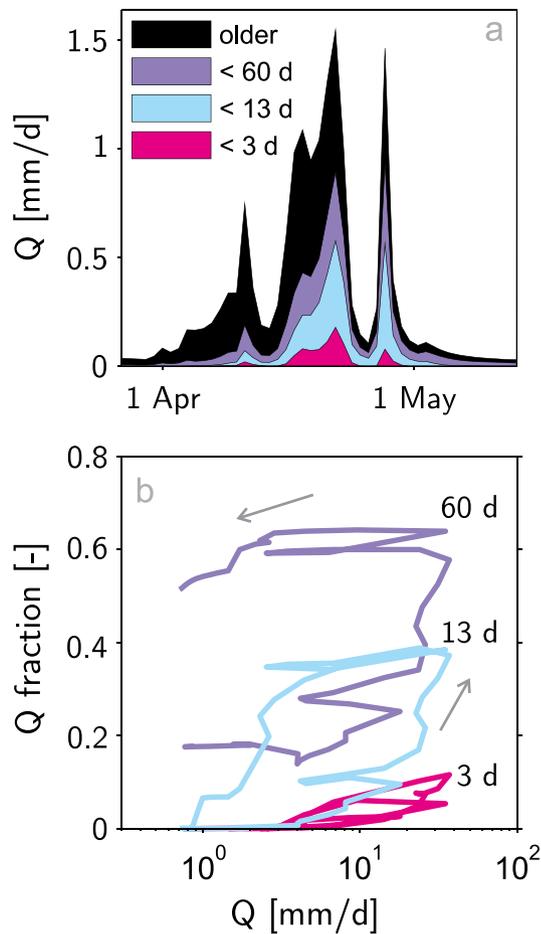


FIGURE 2 Stream age dynamics as predicted by the model for the selected period during the snowmelt season, 2008. (a) Discharge time series with highlighted fractions of young water (3, 13, and 60 days); (b) selected trajectories in the discharge–young water fraction space

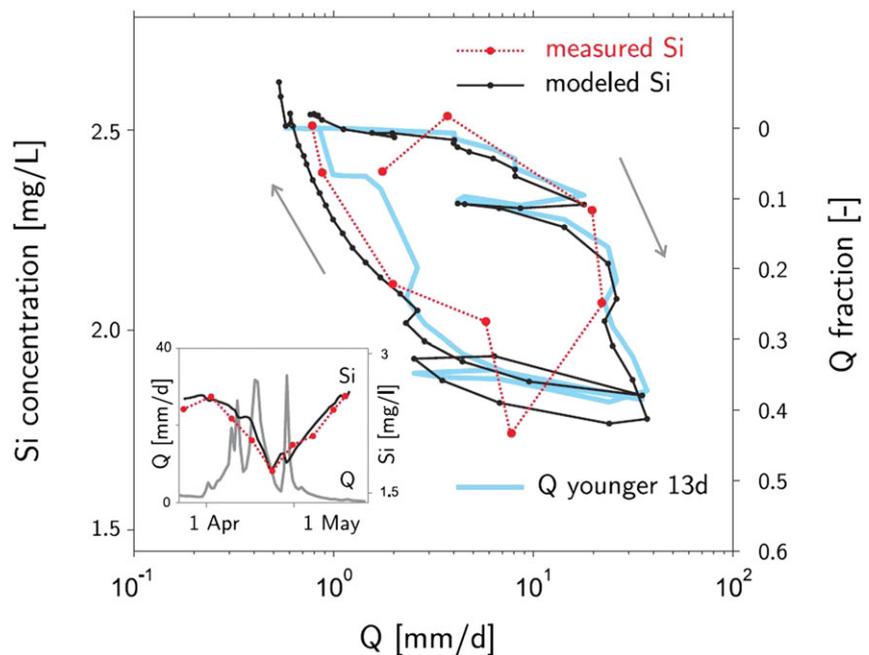
through precipitation and snowmelt; the fraction younger than 13 days is more persistent during this wet period and goes through a complete hysteretic loop (Figure 2b) starting and ending at 0%; the fraction of

water younger than 60 days displays a similar hysteretic loop, but it is shifted upwards and does not close as it has a much longer persistence. We show in Figure 2a that water older than 2 months (black area) is always at least 35% of total discharge, indicating that even during the discharge peaks there is an important contribution of older water (Botter, Bertuzzo, & Rinaldo, 2010; Klaus & McDonnell, 2013). Furthermore, the sources of water contributing to these different age fractions derived from the model suggest different flow paths or portions of the catchment contributing to runoff. The component <3 days old represents precipitation and snowmelt event water moving through shallow, rapid pathways, whereas the older fraction of >60 days represents contributions mainly from groundwater storage.

4 | JOINT DISSOLVED SILICON AND WATER AGE DYNAMICS

The temporal evolution of distinct young water fractions can be directly compared to the measured (and modelled) dissolved Si concentration patterns in the stream water. It is worth noting that the model estimated the age dynamics based on deuterium data only and that the age structure was not further modified or dependent on dissolved Si dynamics. During the considered period, measured dissolved Si concentrations in the stream showed a marked decrease, which was delayed with respect to the discharge peak (Figure 3, inset), hence generating a clockwise hysteresis loop on a concentration–discharge plot (Figure 3, main). Further, the hysteretic behaviour of measured dissolved Si was closely matched by the fraction of discharge younger than 13 days (Figure 3). This result suggests that there is a young water fraction that, independently of any kinetic model, controls the extent and the dynamics of the hysteresis of the measured Si signal. Therefore, such a threshold can be used as a characteristic timescale for catchment-scale conceptualization of Si weathering at HBEF (Benettin *et al.*, 2015), supporting the idea that water significantly older than 2 weeks does not bring additional chemical information to the

FIGURE 3 Joint silicon and age dynamics. (inset) retarded Si dilution with respect to discharge peak; (main) concentration–discharge (left axis) and young flow–discharge (right axis) plots. Si is dissolved silicon concentration; Q is discharge. Measured Si dataset is weekly; modelled Si is daily



measured signal. This result reinforces the ability of the outflows' age structure to summarize key properties of the hydrochemical response of catchments without necessarily relying on a detailed characterization of the internal hydrologic and geochemical heterogeneity of watersheds, but still reflecting their integrated effect.

Clockwise hysteretic loops such as the one shown in Figure 3 are not always observed in Si hydrochemistry as the dilution depression of the chemograph can occur closer (or prior) to the discharge peak (see Godsey, Kirchner, & Clow, 2009). At Hubbard Brook, the physical origin of this result seems to originate from the early mobilization of relatively old water that was stored primarily in riparian areas (Detty & McGuire, 2010), before the contribution of younger water occurs. A similar hysteretic pattern can be observed during other events in the data record, but it is most evident in the analysed spring 2008 period.

5 | IMPLICATIONS FOR WATERSHED FUNCTION

Our approach is based on inferring hydrologic transport against tracer (e.g., deuterium) data and using it to infer patterns of solutes (Si in this case) transported by water. Concentration–discharge relationships are a simple tool widely used in the literature (e.g., House & Warwick, 1998; Karis, Silvester, & Rees, 2016; Likens, 2013; Thompson, Basu, Lascurain, Aubeneau, & Rao, 2011) and our findings suggest the opportunity to compare them to age–discharge relationships. A meaningful metric for water age is the fraction of young stream water, where different degrees of young can be assessed and related to different solutes. The approach is expected to hold for the more mobile and weakly sorbing solutes (see Evans & Davies, 1998) whose concentration dynamics in streamflow are strongly influenced by the catchment hydrologic conditions. Other works such as Tunaley, Tetzlaff, Lessels, and Soulsby (2016) suggest a relationship between the median water age and dissolved organic carbon concentration, although the biological component of dissolved organic carbon processing, which is often independent of hydrologic transport, makes it less evident.

Characterizing solute dynamics through the behaviour of selected water age thresholds is a promising avenue for furthering our insight into catchment transport phenomena. This paper provides a proof of concept that the characterization of young water fraction dynamics summarizes the coevolution of discharge and solute concentrations (both in terms of magnitude and timing). Therefore, age dynamics could be used to predict the form and nature (say, clockwise vs. counterclockwise) of hysteretic loops in the concentration–discharge relation for different types of solutes. Our exercise also suggests that such relationships should be utilized to drive the calibration of hydrochemical models because they imply a robust assessment of the age structure of the outflows, with notable implications for identifying legacy effects on catchment solute delivery.

The application to dissolved Si at Hubbard Brook suggests a potential of the approach for hydrochemical process understanding. Mineral weathering is a critical process that drives the development of soil, is the primary consumer of acidity, and provides many required nutrients for ecosystem function. Estimates of nutrient losses from ecosystems through stream water export are critical in addressing

questions related to the sustainability of forest management (e.g., forest harvest; Vadeboncoeur *et al.*, 2014) and understanding how watersheds recover from decades of air pollution (Burns *et al.*, 2011; Likens, 2013). By including tracers and water age estimates in models, time dependence of weathering rates can be evaluated and used to improve understanding and management of ecosystem function.

Overall, the significance of the approach lies in the proof that widely observed patterns such as concentration–discharge hysteresis can be related to the time variability of streamflow age. The young water fractions can be seen as functions that integrate short hydrologic pathways; hence, their temporal evolution reflects the time variability of runoff generation processes. Therefore, the quantification of young runoff components can be used to identify the expected response of catchments to changes in the underlying hydrologic drivers (e.g., rainfall input and vegetation) and the time lags between implementation of best management practices and related improvements in water quality.

6 | CONCLUSIONS

The proposed framework is used to simultaneously express the dynamics of water age and solute concentration in response to rainfall or snowmelt events. Although solute transport dynamics across a hydrologic domain are complex and heterogeneous, this study emphasizes the simplicity of catchment-scale metrics such as water age, which integrate the bulk effects of the relevant heterogeneity of hydrologic and chemical processes, and fosters the joint analysis and interpretation of chemical and hydrologic responses of catchments. The main results can be summarized as follows:

- Water of different ages has different dynamics and different contributions to streamflow, with the younger components (i.e., days to few months) playing a major role in explaining solute concentration variations.
- Computing the fraction of water younger than some threshold is a useful diagnostic tool to describe hydrologic transport, and it is less influenced than other metrics by the uncertainty of the old water components.
- The fraction of water younger than roughly 2 weeks (13 days) simulated by the hydrochemical model closely resembles the evolution of the observed dissolved Si concentration at HBEF during spring 2008.
- Although applied here to one specific solute (Si), the framework can be tested on other relevant solutes to infer the characteristic timescales of their export to the stream.

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