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Modelling transport of dissolved silica in a forested headwater catchment: the effect of hydrological and chemical time scales on hysteresis in the concentration–discharge relationship

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Abstract:

The relationship between concentration c and discharge Q in a stream is one of the aspects of hydrochemical catchment response that has been used widely as a diagnostic. In particular, loops in the $c-Q$ curve, commonly referred to as hysteresis loops, are used to infer particular mixing patterns. At the South Fork of Brokenback Run (SFBR) in the Shenandoah National Park, Virginia, we have evidence that stream dynamics reflect a system composed of an ephemeral subsurface stormflow zone perched above a perennial water table. The relationship between dissolved silica and stream discharge exhibits hysteresis in the clockwise (CW) direction. Modelling this relationship in the context of three-component mixing with constant-concentration end members failed to reproduce the observed $c-Q$ pattern. In this paper we examine the possibility that temporal variation in soil-water concentrations of silica can explain how CW hysteresis loops in the $c-Q$ curve can arise. In particular, we examine the role of the ratio of a hydrological time scale to a chemical time scale in determining the nature of hysteresis loops. The CW loops that we observe in SFBR can be explained by time variability in soil-water concentrations only if the chemical (leaching) time constant is less than (or only slightly greater than) the hydrological time constant. The near equality of these time constants is consistent with reports from hydrological measurements and leaching experiments. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS concentration–discharge relationships; hysteresis; hydrological tracers; silica transport

INTRODUCTION

The use of chemical tracers in catchment hydrology is an essential part of the science (e.g. Kendall and McDonnell 1998). The interpretation of results of tracer measurements is not always straightforward, however. When tracers are used to infer flow paths and residence times in a catchment, a model of the hydrological system is required. That is, the data are used in an inverse solution to infer parameters of the underlying conceptual–mathematical model, which may be a simple two-component mixing model or may be much more complex. Problems arise because the proper model may not be known, because the inverse solution may not be unique, and because data may not be adequate to constrain the solution (e.g. Rice and Hornberger 1998). Even relatively simple relationships between flow and chemical composition in a stream may be consistent with a variety of assumptions about flow paths and composition of water of the assumed mixing components.

One approach that has been taken to extracting generalizations from data in the face of the difficulties with strict inverse procedures is an examination of patterns rather than precise time series of data. The relationship

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between concentration c and discharge Q in a stream is one of the aspects of hydrochemical catchment response that has been used widely as a diagnostic. In particular, loops in the $c-Q$ curve, commonly referred to as hysteresis loops, are used to infer particular mixing patterns. Evans and Davies (1998) demonstrate that a range of patterns in $c-Q$ curves can be explained using simple two- and three-component mixing models.

Interpretations of $c-Q$ curves using a three-component mixing model most often are based on the assumption that concentrations in each component are space and time invariant. According to Bonell (1998), 'the assumption that the concentration of each component remains constant during a storm event continues to provide the largest uncertainty' in analyses based on the mixing model.

In forested headwater catchments, the flow components most often invoked in mixing models are ground water, soil water, and saturation overland flow. In some catchments, a region of perched water can form in the shallow subsurface, leading to rapid and significant contributions from a shallow subsurface (soil-water) component (Hammermeister *et al*., 1982; Chappell *et al*., 1990; Mulholland, 1993; Brown *et al*. 1999). Rapid changes in saturation following relatively dry interstorm periods can mobilize solutes that have accumulated in the soil. In many cases these solutes can be depleted over the course of a storm, leading to time variation in the concentration of the shallow subsurface stormflow component; the solutes are 'flushed' to the stream (Walling and Foster, 1975; Evans and Davies, 1998). Temporal variations in ground water over the course of a rainstorm are typically taken to be negligible. Buttle and Peters (1997) report dilution of silica in near-bedrock water during a large event, however. The overland flow component is considered as an input to the stream from direct fall on the stream surface and from flow from saturated areas. It is essentially impossible to measure concentrations representative of overland flow or even to determine what 'average' concentration should be used in mixing models (Anderson and Burt, 1982; Robson *et al*. 1992).

At the South Fork of Brokenback Run (SFBR) in the Shenandoah National Park, Virginia, we have evidence that stream dynamics reflect a system composed of an ephemeral subsurface stormflow zone perched above a perennial water table. The relationship between dissolved silica and stream discharge exhibits hysteresis in the clockwise direction. We implemented a version of TOPMODEL that incorporates the shallow zone with an ephemeral perched water table in addition to a ground-water zone (Scanlon *et al*., 2000) and used predicted flows with a three-component mixing model to examine $c-Q$ relationships (Scanlon *et al*., 2001). Using time-invariant concentrations, we found that clockwise hysteresis could not be reproduced without making unreasonable assumptions about the concentration in the shallow subsurface stormflow and in the overland flow components.

In this paper we examine the possibility that temporal variation in soil-water concentrations of silica can explain how clockwise hysteresis loops in the $c-Q$ curve can arise. In particular, we examine the role of the ratio of a hydrological time scale to a chemical time scale in determining the nature of hysteresis loops. Duffy and Cusumano, 1998, use a ratio of hydraulic relaxation time to solute residence time as a key parameter for describing $c-Q$ behaviour with a simple reservoir model. Our results suggest that the nature of the observed loops in $c-Q$ curves for silica in small catchments that have a mechanism whereby water flowing through shallow soils can move rapidly to the stream, may be determined by a ratio of a hydrological time scale to a leaching time scale.

BACKGROUND

Field studies

Our study site is the catchment drained by the SFBR, on the north side of Old Rag Mountain, Shenandoah National Park, Virginia (Figure 1). The 237 ha catchment drained by SFBR lies within the Rappahannock River Basin and is undeveloped. A soil and saprolite regolith is developed on top of the Precambrian Old Rag granite that underlies the entire catchment. The granite is a coarse-grained porphyritic rock composed mainly of perthitic microcline and quartz (Gathright, 1976). Saprolite development is similar to the Virginia Piedmont

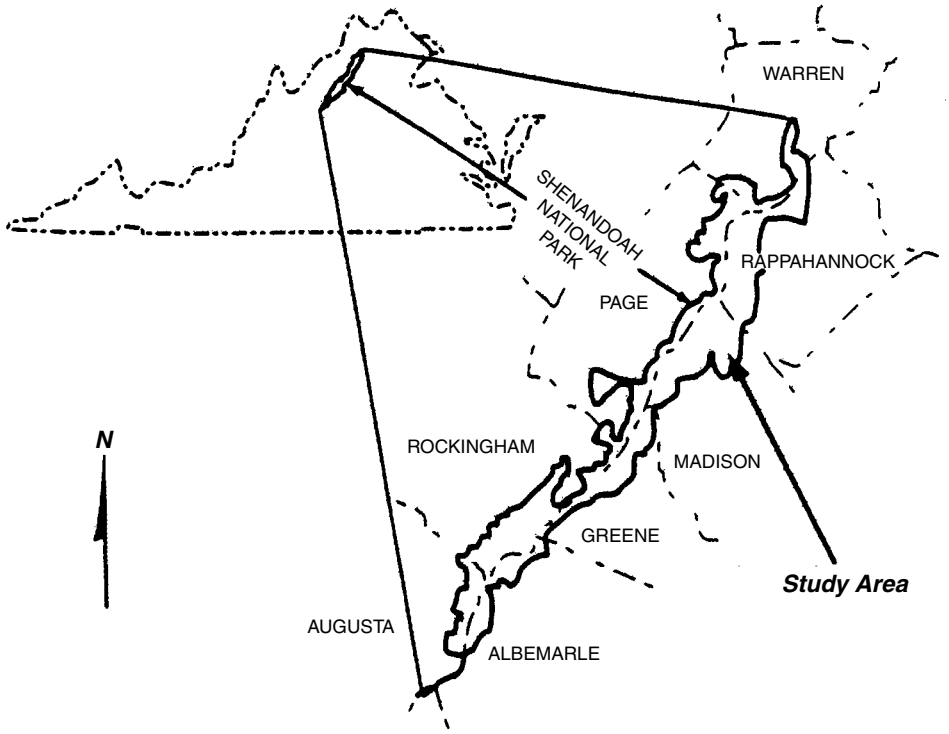

Figure 1. Location map for the catchment drained by SFBR. The area outlined by the solid line is Shenandoah National Park

catchment studied by Pavich (1986), and may be thicker than 20 m on some sideslopes (O'Brien *et al*., 1997), although bedrock is exposed in resistant outcrops throughout the catchment, including the stream bed.

Precipitation, stream discharge, temperature, and humidity were measured at the site. Data from a transect of shallow piezometers indicated that a perched water table develops at the site during many storms. Overland flow collectors showed that saturated areas develop in the riparian zone during events. (See Scanlon *et al*., 2000, for details of the field procedures at the site.)

Silica concentrations in the stream were measured for several storm events (Scanlon *et al*., 2001). Loops in the $c-Q$ plots were clockwise, i.e. silica concentrations were higher on the ascending limb of the hydrograph than on the descending limb for equal stream discharge. Silica concentrations were also measured in water collected from shallow tension lysimeters (Greene, 1997). The six lysimeters were installed to a depth of approximately 0·4 m below the ground surface were all more than 5 m from the stream. These lysimeters were taken to represent water that would be flushed from the shallow subsurface stormflow zone. Also, throughfall was collected and concentrations were measured.

Application of TOPMODEL

Scanlon *et al*. (2000) report the application of a version of TOPMODEL that includes two subsurface components, one representing the perennial ground-water zone and the other the shallow subsurface stormflow zone with an ephemeral perched water table. The water-balance accounting in each subsurface zone follows the saturation deficit approach of the standard TOPMODEL (Beven and Kirkby, 1979). The model resolves the total stream discharge into flow components from ground water, shallow subsurface stormflow, and saturation excess overland flow (Figure 2).

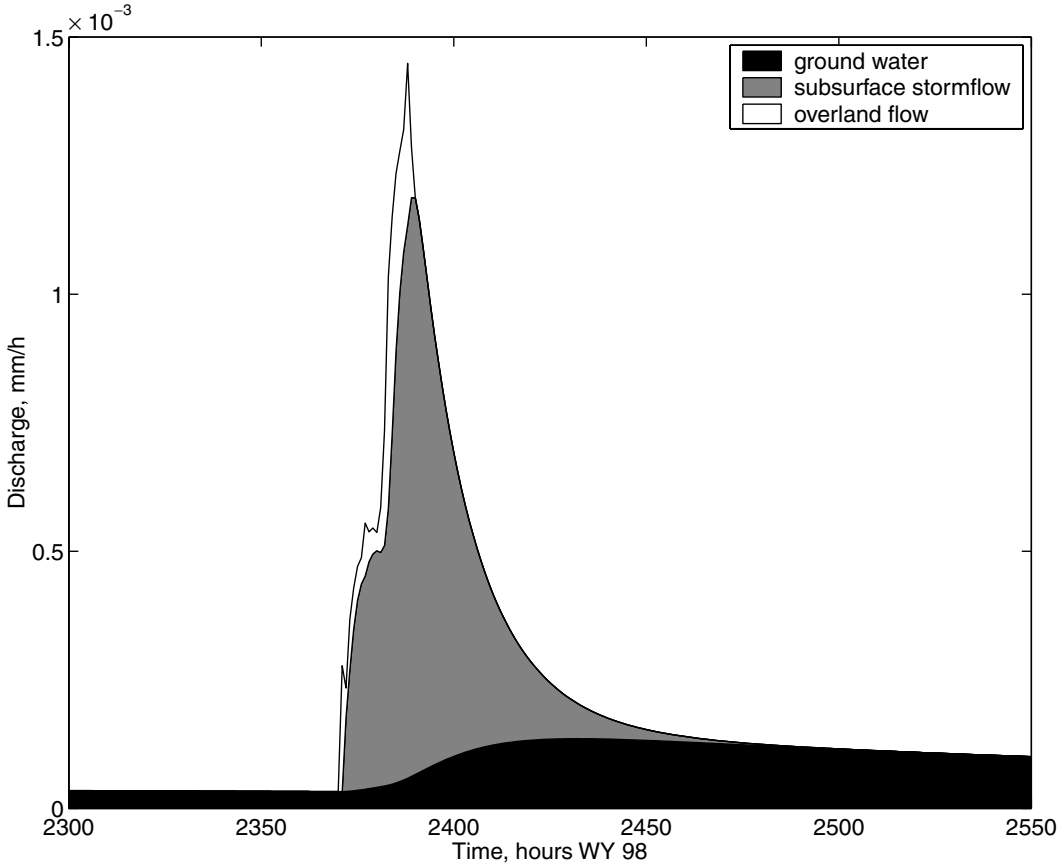

Figure 2. Hydrograph components simulated with the modified TOPMODEL of Scanlon *et al*. (2001a)

A three-component mixing model

Scanlon *et al*. (2001) applied the modified TOPMODEL to examine silica variations in stream water. Leaching experiments from samples from a core through the saprolite indicated that silica concentrations should increase with depth below the water table. After 21 days of leaching, silica concentrations ranged from about 4 mg l^{-1} near the surface to about 14 mg l^{-1} at a depth of 23 m (Scanlon *et al*., 2001). Scanlon *et al*. (2001) accounted for depth variation of silica concentration in the ground-water zone by specifying the concentration as a function of the spatially averaged saturation deficit. (Mass accounting in the groundwater store in the modified TOPMODEL uses the concept of saturation deficit in that zone. In this instance, the saturation deficit is the amount of water that would need to be added to raise the water table to the surface.) The increase in silica concentration with depth in the saturated zone was reflected in the relationship between concentration and discharge for samples taken at baseflow. That is, silica concentrations in streamwater increase with decreasing discharge at baseflow. The model for ground-water variation in silica was set to reproduce the observed variation over base flow periods (Scanlon *et al*. 2001). The resulting model calculations were consistent with the data from the leaching experiments run on the saprolite core material (Scanlon *et al*. 2001). Silica concentrations in soil water display very little temporal variation, but tend to increase downslope (Greene, 1997). Silica concentration was taken to be constant in shallow subsurface stormflow and also taken

to be constant for overland flow. The concentration for overland flow was not known,[1] so was set equal to the mean of the concentration measured in throughfall and that measured for soil water. The results from the modelling exercise showed a 'reasonable' dilution pattern over the course of a storm, but a $c-Q$ loop that went in the counter-clockwise direction (Scanlon *et al*., 2001). One possible explanation for the inconsistency in the mixing model is that time variation in the soil-water concentration may be important. Buttle and Peters (1997) report that silica concentrations in water from suction lysimeters remained sensibly constant, although concentrations in water actually moving through the soil decreased and then recovered over the hydrograph.

METHODS

Our aim is to examine the possibility that time variations in silica concentration in the shallow subsurface zone at SFBR might explain the observed clockwise pattern in $c-Q$ plots. In particular, we ask whether the notion of a ratio of a hydrological time scale to a chemical time scale, as proposed by Duffy and Cusumano (1998), distinguishes between looping directions produced by a mixing model based on the flows constructed with the modified TOPMODEL.

We consider a very simple model for variation of concentration in the shallow subsurface stormflow, assuming the component to be a mixed reservoir.

$$\frac{\mathrm{d}(cV)}{\mathrm{d}t} = Q_\mathrm{b}(c_\mathrm{in} - c) + \alpha(c_\mathrm{max} - c)V \tag{1}$$

where c is the silica concentration in the shallow subsurface stormflow, V is the volume of water in the shallow subsurface stormflow zone, t is the time, Q_b is the flow rate through the shallow subsurface stormflow zone, c_in is the silica concentration in infiltrating water, α is the silica leaching rate constant, and c_max is the maximum attainable silica concentration in soil water.

Our simple treatment of the leaching process is motivated by the shape of curves describing the time course of the increase of silica concentrations in batch soil leaching experiments (e.g. McKeague and Cline, 1963). Such curves suggest that, to a first approximation, silica concentrations approach some 'maximum' value and that the approach can be characterized using a first-order rate constant [α in Equation (1)]. The actual process is undoubtedly much more complex than this, but the formulation suffices for our examination of possible effects of transients in concentration on the form of the concentration–discharge relationship.

Equation (1) can be rearranged:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{Q_\mathrm{b}}{V}(c_\mathrm{in} - c) + \alpha(c_\mathrm{max} - c) - \frac{c}{V}\frac{\mathrm{d}V}{\mathrm{d}t} \tag{2}$$

Finally, we assume that the flushing (hydraulic) time constant for the subsurface stormflow store, V/Q_b, is inversely proportional to Q_b. (The hydraulic time constant is the time it would take the concentration in the store to decrease to about 0·63 of its initial value given a constant flow rate in the absence of any additions from leaching.) The assumption is that the stormwater zone flushing time decreases with Q_b and that a simple linear relationship suffices to describe this dependency. Also note that the volume changes in the store can be related to the changes in saturation deficit S calculated in TOPMODEL. The equation for the time-varying concentration in the shallow subsurface stormflow zone is then:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \gamma Q_\mathrm{b}(c_\mathrm{in} - c) + \alpha(c_\mathrm{max} - c) + \frac{c}{S}\frac{\mathrm{d}S}{\mathrm{d}t} \tag{3}$$

where γ is a hydraulic time constant per unit discharge and S is the saturation deficit of the subsurface stormflow zone.

[1] The overland-flow collectors that we used were to determine only the presence or absence of overland flow at a location. The collectors could not be used for quantitative measurements of either flow or chemical composition.

Values of the parameters α and γ were chosen to cover a fairly broad range. Time constants for flushing of dissolved organic carbon in shallow suction lysimeters were found to be on the order of 10 days by Boyer *et al*. (1997) for an alpine catchment. For a shallow subsurface stormflow zone discharge of about 3×10^{-4} mm h^{-1}, a value of γ of about 10 mm^{-1} would be indicated under these conditions. We anticipate that shorter time constants (larger values of γ) are probably more appropriate for SFBR. We used a range from 15 to 165 mm^{-1} in Monte Carlo simulations with our model to examine the importance of parameter variations. Values of α were selected to range from 0·008 to 0·088 h^{-1} for the simulations. (The time constants are the reciprocals of these values, ranging from about 11 to 125 h.) Laboratory leaching experiments typically suggest time constants on the order of hours to tens of hours (e.g. Kennedy, 1971; Smith and Dunne, 1977), but laboratory rates often overestimate those appropriate for field conditions (e.g. Swoboda-Colberg and Drever, 1993).

Some 200 Monte Carlo realizations were run using our simple chemical model [Equation (3)] with the modified TOPMODEL of Scanlon *et al*. (2000) and the storm period from 2300 h to 2550 h in water year 1998 (Figure 2). Parameter values for α and γ were selected from uniform random distributions with the bounds indicated above. Results were characterized as having a clockwise $c-Q$ loop (CW), a counter-clockwise $c-Q$ loop (CCW), or as being ambiguous (displaying a 'figure of eight' pattern) with regard to the loop direction. The assignment was made on the basis of the concentration on the ascending limb being above or below the concentration on the descending limb at discharges of one-third and two-thirds of the maximum value.

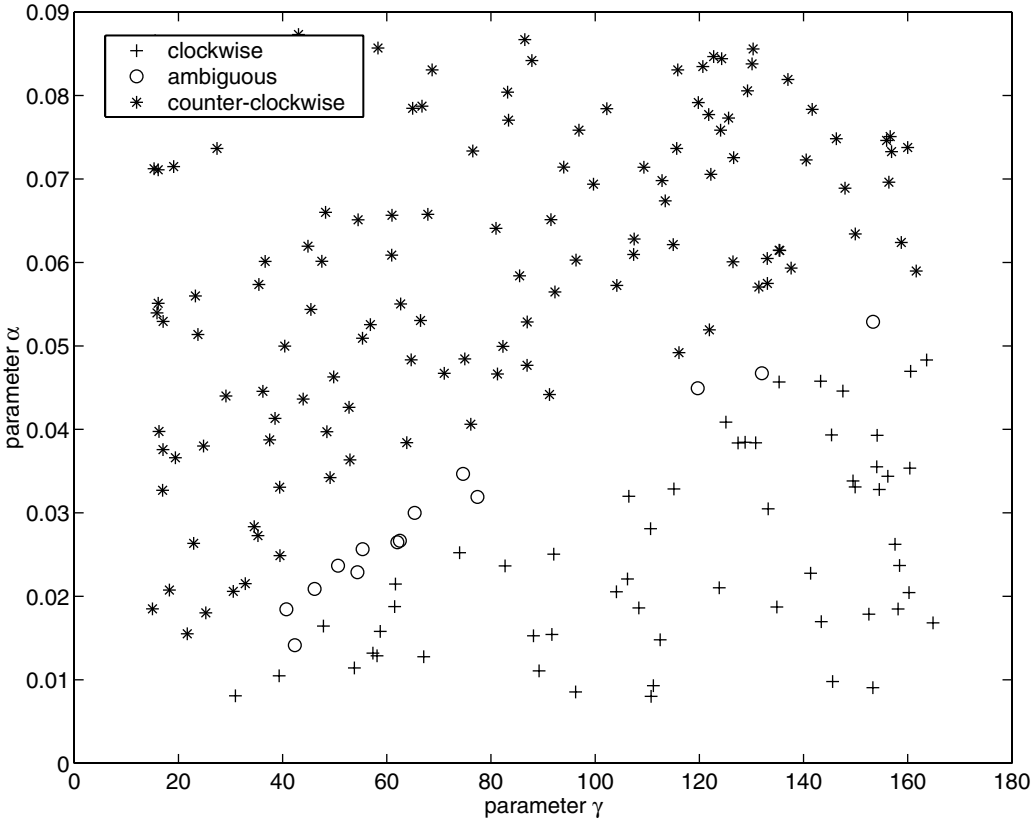

Figure 3. Parameter map for different directions in $c-Q$ loops for 200 Monte Carlo realizations

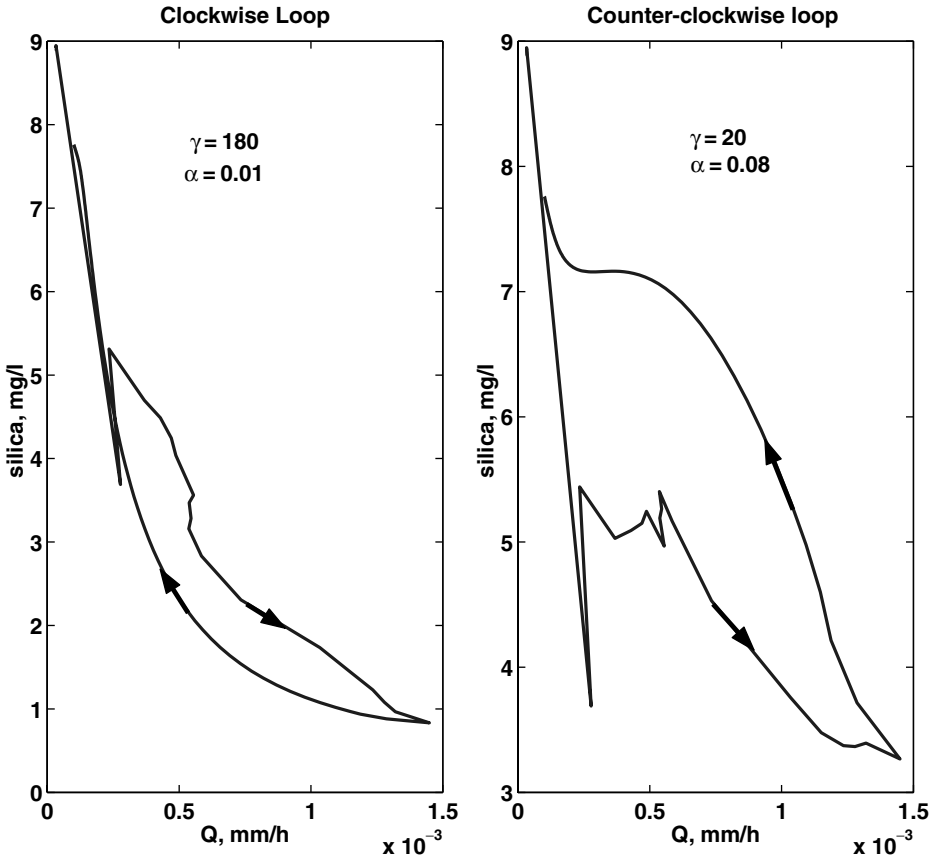

Figure 4. Representative $c-Q$ plots for parameter values that give CW and CCW loops

RESULTS

The parameters for realizations that showed a CW loop separated distinctly from those showing a CCW loop (Figure 3). Large values of γ combined with small values of α favoured CW loops with the reverse for CCW loops (Figure 4).

We defined a new parameter, β, to represent a hydrological time constant for the system. This parameter was calculated by multiplying γ by the mean value of Q_b for the storm. (Recall that γ is a time constant *per unit discharge*.) The ratio α/β is then a measure of a chemical time constant to a hydrological time constant for the SFBR simulation. The hydrological time constant is a characteristic time for dissolved material to be flushed from the soil by water flowing through it (e.g. Hornberger *et al*. 1994). The chemical time constant is a characteristic time for silica to be replenished in soil water by a leaching process. Simulation results suggest that values of this ratio above about 1·5 lead to CCW loops and values below this threshold lead to CW loops (Figure 5).

DISCUSSION

Silica has been used widely as a hydrological tracer in small catchments (e.g. see Buttle and Peters (1997), and references cited therein). A chief assumption in using silica is that water that infiltrates into the soil attains a constant concentration that is a signature of the flowpath. Both field measurements and laboratory

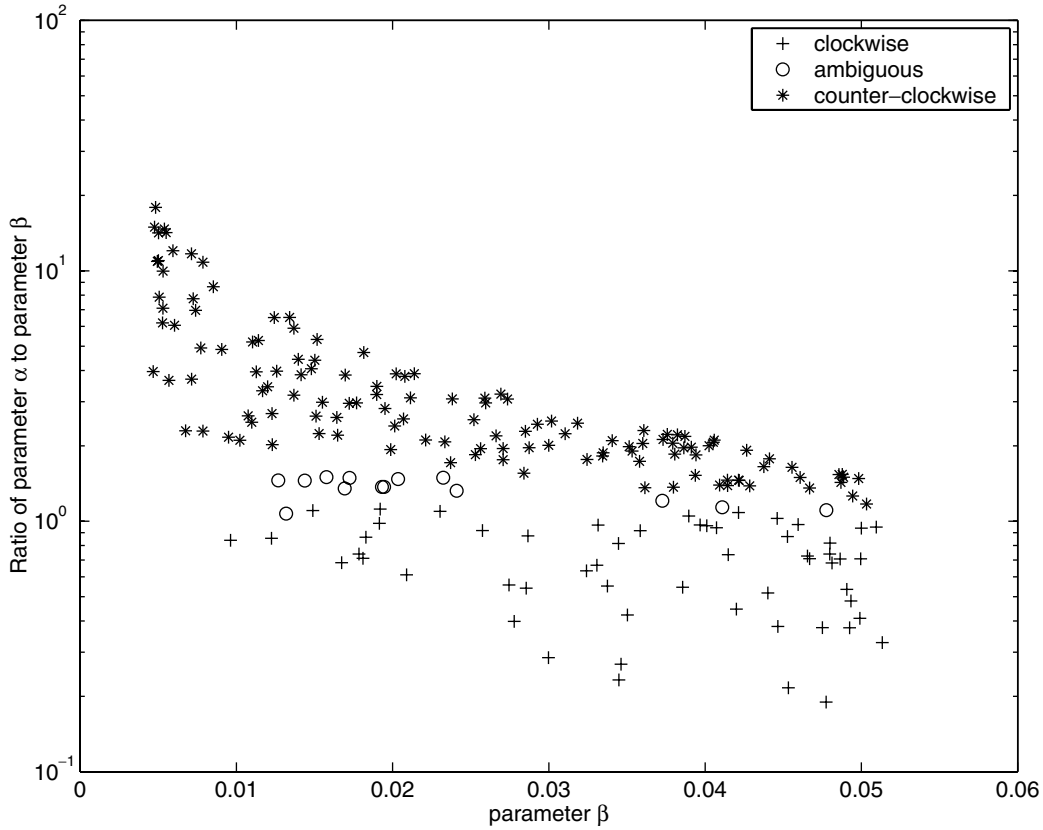

Figure 5. CW and CCW $c-Q$ plots are distinguished by a threshold value of the ratio of the leaching time constant to a hydrological time constant

leaching experiments have been used to support this supposition (Maulé and Stein, 1990; Wels *et al*., 1991). The argument is that silica concentrations increase rapidly and then stabilize, usually within a period of hours or at most a day (Kennedy, 1971; Wels *et al*. 1991).

In catchments in which perched water in a shallow soil develops, the delivery of water to the stream can be quite rapid, especially in small catchments (Brown *et al*. 1999), and this shallow subsurface stormflow can be a major delivery mechanism for solutes to the stream (Chappell *et al*., 1990). In such cases, the rate at which water flushes the zone may be rapid even with respect to leaching rates for silica. For example, Buttle and Peters (1997) report that 'silica levels in hillslope discharge varied with time, reflecting dilution by silica-poor event water combined with water fluxes in excess of the rate at which silica was released to runoff from soils and the bedrock surface'.

The results of our modelling study suggest that looping patterns in observed $c-Q$ curves in a catchment in which a shallow perched water table transports water rapidly to the stream may be determined by a ratio of a leaching time constant to a hydrological time constant (Figure 5). Duffy and Cusumano (1998) show a variety of $c-Q$ looping patterns in response to varying a dimensionless ratio that in their model represents the ratio of a solute residence time to a hydraulic relaxation time. We cannot compare our results directly with those of Duffy and Cusumano (1998) because they modelled dilution (or enrichment) in a single reservoir, whereas we use three components at SFBR. Nevertheless, our results support the general notion that a dimensionless ratio of hydrological and chemical time scales can be useful in a general characterization of possible catchment behaviour.

The CW loops that we observe in SFBR can be explained by time variability in soil-water concentrations only if the leaching time constant is less than (or only very slightly greater than) the hydrological time constant. For rapid response systems like the perched stormflow zone in SFBR, it can be argued that the hydrological time constant must be on the order of hours or tens of hours. If CW loops are to be simulated by our model under these conditions, the leaching rate constant for silica and the hydrological time constant have to be on the same order, an assumption that is not at odds with reports from field measurements and leaching experiments.

If the time constant for leaching is very small, dilution of the soil water (or ground water) may lead to very slow recovery to initial concentrations after a storm. As noted by Evans and Davies (1998), if weathering (or leaching) fails to 'keep up' with flow, the result will be a characteristic open-ended $c-Q$ loop. In very large storms, we have observed open-ended $c-Q$ loops in silica at SFBR (Greene, 1997). The failure to return to pre-storm concentrations of silica in the stream persists well beyond the time when the shallow stormflow zone is active, however. Thus, the dilution effect must be in the perennial ground water. Alternatively, the open-ended loop may not be due to dilution *per se*, but rather may be attributable to the fact that silica leaching varies strongly with depth below ground surface (Scanlon *et al*., 2001b). Raising the water table produces baseflow to the stream that has a lower silica concentration, so concentrations return to pre-storm levels on the time scale of lowering of the perennial water table, a process that is much slower than drainage of the shallow stormflow zone. This indicates that spatial variations in concentrations can affect the pattern of $c-Q$ loops as well as can temporal variations.

It is a truism that an understanding of the hydrochemical behaviour of any catchment can be had only by careful and detailed measurements of both flows and chemical compositions (e.g. Elsenbeer and Lack, 1996; Bonell, 1998). Nevertheless, simple models will undoubtedly continue to form the basis for inferences made from measurements at small catchments. With regard to inferences using $c-Q$ plots, Evans and Davies (1998) show that loops of different shapes, and with either CW or CCW directions, can be produced from mixing time-varying proportions of water from three sources with constant concentrations. This procedure for interpreting field data will undoubtedly (and deservedly) continue to be the norm. Our results suggest, however, that there are certain cases for which a more complex conceptual-mathematical model, which accounts for solute residence times and for leaching times, will be needed to explain patterns in $c-Q$ curves.

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