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Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry

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Abstract. Episodic variations in dissolved solutes are frequently complicated by a cyclical relationship between concentration and stream discharge. Established three-component models of runoff generation are used to explain this hysteresis effect and to illustrate how different component concentrations produce different hysteresis forms. It is demonstrated that a two-component model cannot reproduce all the hysteresis forms commonly observed. A method, based on the three-component system, is derived by which C/Q hysteresis can be used to predict relative component concentrations. This may provide a qualitative chemical description of sources supplying runoff for locations where these have not yet been directly established or a validation test where possible components have been sampled. The method has been tested using data collected at streams in the Adirondacks, New York, and the Northern Appalachian Plateau, Pennsylvania, during the Episodic Response Project of the U.S. Environmental Protection Agency. Predicted component compositions were in good agreement with measurements made during other studies and with those subsequently obtained from one of the Pennsylvania watersheds.

1. Introduction

Much of the chemical variation in streamwater occurs in response to periods of increased discharge. However, despite there frequently being a clear response of concentration (C) to discharge (Q), this rarely takes a simple linear or curvilinear form [*Walling and Webb*, 1986]. *Hendrickson and Kreiger* [1964] and *Toler* [1965] observed cyclical relationships between discharge and concentration of dissolved solids, whereby the concentration at a given discharge on the rising limb of the hydrograph differed from that at the same discharge on the falling limb. This hysteresis in the episode C/Q relationship has since been observed by numerous authors in the United Kingdom [*Oxley*, 1974; *Johnson and East*, 1982; *Walling and Webb*, 1986], Norway [*Johannessen et al.*, 1980] and U.S. [*Miller and Drever*, 1977; *Bond*, 1979; *Swistock et al.*, 1989; *Hooper et al.*, 1990; *Hill*, 1993; *Shanley and Peters*, 1993].

C/Q hysteresis occurs whenever there is a difference in the relative timing or form of solute and discharge responses [*Walling and Webb*, 1986]. *Walling and Foster* [1975] suggested that observed hysteresis (in the form of lagged solute responses) might be due to the early episode flushing of soluble material. It has since been recognized that hysteresis can also result from component mixing processes [*Swistock et al.*, 1989; *Hooper et al.*, 1990]. This study will use a simple modelling approach to examine the relationship between component mixing and C/Q hysteresis, primarily in terms of the three-component model (3CM). An assessment will also be made of the extent to which the simpler two-component model (2CM) can generate the same results. Methods are developed which relate the form of a hysteresis loop to the relative concentration of different source components, and these are tested using data collected at streams in the Adirondacks, New York, and the Northern Appalachian Plateau, Pennsylvania, during the U.S. Environmental Protection Agency's Episodic Response Project (ERP) [*Wigington et al.*, 1996]. The ERP included intensive episodic streamwater sampling but did not monitor possible source components such as soil water or throughfall. A method for predicting component compositions using stream data would thus be a valuable addition to this study. Results are compared with those from other studies and with the results of recent sampling of one of the original ERP streams to assess whether the methods developed provide realistic results.

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2. Methods

2.1. Modelling Runoff Using a Three-Component System

The 2CM generally considers "event" and "pre-event" water sources. Event water usually equates to precipitation or throughfall, with pre-event water representing stored subsurface water of uniform chemical/isotopic composition. However, in systems where water from the soil zone makes a significant and chemically/isotopically distinct contribution to runoff, it is necessary to consider this as a third component [*Kennedy et al.*, 1986; *DeWalle et al.*, 1988a]. A number of studies have employed some form of 3CM, including those of *DeWalle et al.* [1988a], *Swistock et al.* [1989], *Hooper et al.* [1990], *McDonnell et al.* [1991], *Ogunkoya and Jenkins* [1993], *Hinton et al.* [1994], *Bazemore et al.* [1994], *DeWalle and Pionke* [1994], *Jenkins et al.* [1994], and *Elsenbeer et al.* [1995a]. All of these studies consider groundwater/base flow and mineral soil water components. In most cases the third component can be loosely defined as "surface event" water, consisting of direct channel interception and/or saturation overland flow (SOF). This is commonly assumed to retain the composition of precipitation in grassland catchments or of throughfall in forested basins, although chemical interaction with surficial materials has been shown to occur during overland flow by *Hill* [1993] and *Elsenbeer et al.* [1995b]. *Elsenbeer et al.* [1995a] measured SOF to represent surface event water, while *Hooper et al.* [1990] identified organic soil water as a third component.

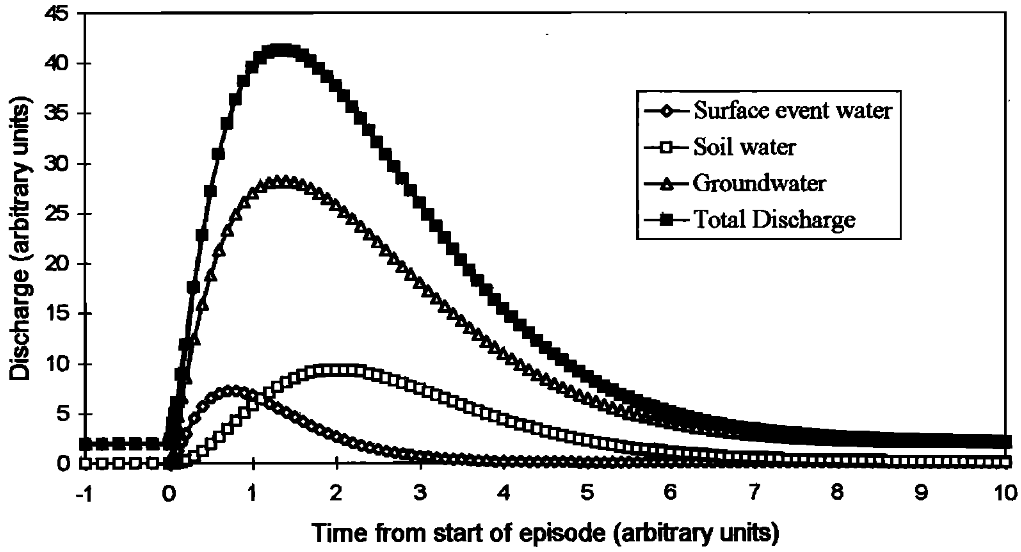

Figure 1. Synthetic episode hydrograph used to model C/Q loops.

For a 3CM of groundwater, soil water, and surface event water components, the concentration of a conservative solute in streamwater at a given time is described by the following mass balance equation:

$$C_T Q_T = C_G Q_G + C_{SO} Q_{SO} + C_{SE} Q_{SE} \quad (1)$$

where C is concentration, Q is discharge, and the subscripts T, G, SO, and SE represent total streamflow, groundwater, soil water, and surface event water, respectively. The methods developed here require only that C_T and Q_T are measured. Provided an event follows a period of low flow, C_G can be approximated by the pre-event C_T. Three-component hydrograph separations require measurement of the two "stormflow components," C_{SO} and C_{SE}, but these are treated here as unknowns. Since component discharges are also unmeasured, precise values for C_{SO} and C_{SE} cannot be calculated. However, by making certain assumptions regarding the nature of hydrograph response, it is possible to obtain estimates for C_{SO} and C_{SE} relative to C_G and to each other so as to determine "component rankings."

An empirically based runoff sequence is assumed for this study. It is essentially that described for Mahantango Creek, Pennsylvania, where a typical progression of dominance during stormflow is believed to be (1) base flow, (2) channel precipitation and SOF (surface event water), (3) shallow subsurface flow (soil water), and (4) base flow [*Pionke et al.*, 1988; *DeWalle and Pionke*, 1994]. Other studies in Pennsylvania by *Swistock et al.* [1989] and *Fulcar* [1990] have observed the same sequence, as have *Hinton et al.* [1994] for a June event at Harp 4-21, Ontario. *Sklash and Farvolden* [1979] found two components to be sufficient for streams in Quebec and Ontario but predict that in a three-component system, event water would be most important on the rising limb and vadose soil water on the falling limb. Consistent with these and other studies, groundwater response is assumed to be large and (as a result of its overall dominance) closely correlated to total discharge.

It is acknowledged that this model may not be universal: at Allt A'Mharcaidh, Scotland, Q_{SE} and Q_{SO} peaks tend to coincide [*Ogunkoya and Jenkins*, 1993; *Jenkins et al.*, 1994], and in one of two events monitored at South Creek, Queensland, by *Elsenbeer et al.* [1995a], timings for these components were actually reversed. However, the assumed precedence of surface event water is consistent with the variable source area concept, in that flow from direct precipitation onto saturated areas peaks before subsurface flow [*Dunne and Black*, 1970; *Hewlett and Nutter*, 1970]. This system is likely to operate widely in humid forested basins. It also seems reasonable to expect soil water response to be lagged, given that a large proportion is likely to derive from hillslope areas, away from the stream network, and that conditions of saturation must usually develop (because of either a rising water table or the development of perched saturation) before significant flow can occur [*Lynch and Corbett*, 1985; *Swistock et al.*, 1989; *Hooper et al.*, 1990]. Groundwater dominance is consistent with ridging theories [*Sklash and Farvolden*, 1979; *Gillham*, 1984] or a simpler mechanism of old water displacement. The sensitivity of the model to changes in assumptions is considered below.

A simple conceptual three-component hydrograph, based on this flow model, is shown in Figure 1. The hydrograph is the hypothetical response to a single-peaked rain input. This was used to generate a set of C/Q plots based on a range of different component concentrations. Components were assigned concentrations of 50, 100, and 150 arbitrary concentration units in a total of six possible combinations.

2.2. Interpretation of C/Q Plots

C/Q plots for each combination of component concentrations are shown in Figure 2. It is apparent that each combination produces a distinct hysteresis loop. Clockwise loops are classed as types C1, C2, and C3, and anticlockwise loops are classed as types A1, A2, and A3. From (1), C_T at a given time will tend towards the flow component which dominates at that time. At base flow, C_T is by definition equal to C_G; on the rising limb it tends towards C_{SE}, and on the falling limb it tends towards C_{SO}. If, for instance, $C_{SE} > C_G > C_{SO}$, C_T will peak on the rising limb and reach a minimum on the falling limb, generating a type C1 loop. The opposite situation ($C_{SO} > C_G > C_{SE}$) will produce the equivalent A1 type anticlockwise loop. If C_{SE} and C_{SO} are both either higher or lower than C_G, that is, C_G is "extreme" rather than "intermediate," one limb

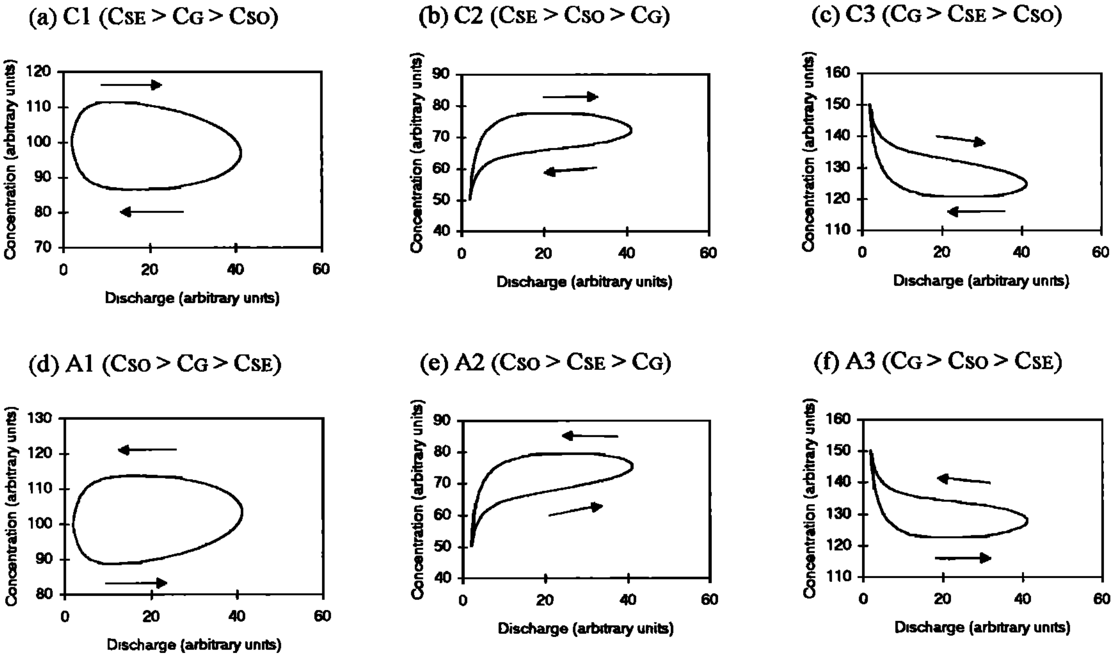

Figure 2. C/Q hysteresis loops created using hydrograph in Figure 1.

becomes partially concave. This occurs because both rising and falling limbs tend away from the base flow value.

Given that each combination of component concentrations produces a distinct and recognisable hysteresis loop, it is proposed that where these forms are observed in real C/Q plots, certain predictions can be made regarding unknown component concentrations. Three basic criteria are needed to characterise the various hysteresis types.

1. Rotational pattern (clockwise/anticlockwise). In any event for which the three-component concentrations differ, a hysteresis loop will occur which can be either clockwise or anticlockwise. In a clockwise loop C_T is higher on the rising limb than on the falling limb. C_{SE} must therefore exceed C_{SO}. With an anticlockwise loop C_{SO} must exceed C_{SE}.

2. Curvature (convex/concave). Technically, all loops must be primarily convex. Here, however, the term is taken to mean that the entire loop is convex. On this basis a "convex" loop implies that on one limb, C_T must tend towards a value greater than C_G, and on the other to a value less than C_G. Thus C_G must be intermediate relative to the other components. Following this definition of convexity, a "concave" loop is one in which all or a significant part of one limb is concave. As discussed above, this implies that C_G must have either the highest or lowest component concentration.

3. Trend (positive/negative). This need only be considered where a loop is concave. A positive trend implies that C_T is consistently higher during the event than it is at base flow, and hence that C_G has the lowest concentration of the three components. A negative trend implies the opposite, that is, that C_G has the highest concentration.

These diagnostic features are together sufficient to place the episodic behavior of a given solute into one of six categories. Each has a unique set of component rankings, as shown in Table 1.

2.3. Hysteresis in a Two-Component System

To some extent, the hysteresis forms observed using a 3CM can also be generated by a 2CM; in this case, pre-event and event water sources are considered, but the observations made are applicable to any two components. For a system in which event water peaks before pre-event water, C_T will be most different to its base flow value on the rising limb. It is thus possible to generate hysteresis types C2 and A3 as shown in Figure 2. If event water is lagged behind pre-event water, types C3 and A2 can be produced. Component rankings for a pre-event/event water 2CM are included in Table 1.

Two-solute mixing plots have previously been used to distinguish between two- and three-component systems [e.g., *DeWalle and Pionke*, 1994]. Deviation from a straight "mixing line" implies a need for a third component. The two systems

Table 1. Diagnostic Features Used to Determine Component Rankings

Type	Rotational Direction	Curvature	Trend	Component Rankings: 3CM	Component Rankings: 2CM
C1	clockwise	convex	N/A	$C_{SE} > C_G > C_{SO}$	N/A
C2	clockwise	concave	positive	$C_{SE} > C_G > C_G$	$C_{EVENT} > C_{PRE\text{-}EVENT}$
C3	clockwise	concave	negative	$C_G > C_{SE} > C_{SO}$	$C_{PRE\text{-}EVENT} > C_{EVENT}$
A1	anticlockwise	convex	N/A	$C_{SO} > C_G > C_{SE}$	N/A
A2	anticlockwise	concave	positive	$C_{SO} > C_E > C_G$	$C_{EVENT} > C_{PRE\text{-}EVENT}$
A3	anticlockwise	concave	negative	$C_G > C_{SO} > C_{SE}$	$C_{PRE\text{-}EVENT} > C_{EVENT}$

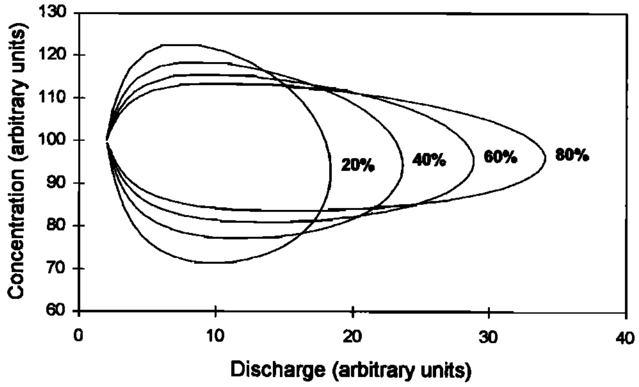

Figure 3. Set of modelled type C1 C/Q plots with varying Q_G and constant Q_{SE} and Q_{SO}. Percentages on plot indicate proportion of peak discharge generated by Q_G. Q_{SE} and Q_{SO} are the same as in Figure 1.

can often also be distinguished using C/Q plots. Most importantly, a simple 2CM cannot generate the convex hysteresis types C1 and A1; this would require that C_T tends towards values both higher and lower than the pre-event value. If any one solute exhibits convex hysteresis, this therefore suggests that a 3CM is necessary. Similarly, a 2CM cannot generate concave loops in combinations other than those given above. If, for example, type C2 and C3 loops occur in the same episode for two different solutes, a 2CM can again be rejected.

2.4. Stability of Modelled C/Q Loops

So far, C/Q plots have been generated for a single three-component hydrograph, using a single set of component concentrations. It is therefore useful to consider the extent to which plots retain a similar form if conditions alter. Three aspects which may vary are component concentrations, component discharge magnitudes, and component discharge timings.

The ranking of component concentrations has already been identified as a critical determinant of hysteresis form. Beyond this, however, absolute component concentrations have no effect on the shape characteristics defined above. The only situations where different forms will arise are special cases in which two components have the same concentrations. If the $C_{SE} = C_{SO}$, plots will approach the curvilinear form shown in Figure 3a. If C_G is equal to one of the other components, the plot will be intermediate between convex and concave forms, so that part of the loop becomes linear (e.g., Figure 3b).

An increase in the magnitude of either Q_{SE} or Q_{SO} will cause C_T to tend more towards the concentration of that component, especially on the limb where it dominates. An elevated proportion of flow from Q_G will reduce the amount by which C_T deviates from its pre-event value, resulting in the "stretching" effect shown in Figure 4. Significantly, no change in component discharge magnitude will affect basic shape characteristics, or subsequent interpretation, in any way. Although a "large" groundwater response was assumed in the model used, then, the exact magnitude of Q_G is unimportant.

The hydrograph model used assumes that Q_{SE} peaks on the rising limb, Q_G peaks at or close to maximum Q_T, and Q_{SO} peaks on the falling limb. Again, any alteration in component discharge timings which does not change this sequence will not affect the shape characteristics of modelled loops. However, if the sequence is altered, hysteresis forms may change significantly. In particular, a reversal of peaks for Q_{SE} and Q_{SO} would change the rotational direction of all loops. This would invalidate interpretation, although as discussed earlier such a scenario is expected to be fairly unusual. A more realistic possibility, observed by *Bazemore et al.* [1994], is that groundwater may be lagged behind soil water. Given that groundwater cannot by itself cause C_T to deviate from pre-episode values, the impact of this change may be limited. However, a large delayed groundwater input is likely to distort C/Q relationships, and the methods described should not be applied to a system in which this situation is thought likely. In practice, it may be possible to identify such a system where inferred component rankings are clearly unrealistic, although obviously this requires some prior knowledge.

2.5. Effects of Temporally Varying Component Concentrations

An inherent assumption of the model used, and of mixing models in general, is that component concentrations remain constant. The violation of this assumption will only affect C/Q forms where component rankings change during the episode. One situation in which this may occur is where soluble material has accumulated prior to the event, for instance because of dry deposition or biologic processes. Flushing is likely to generate high event water concentrations at the start of the episode, followed by exhaustion [*Walling and Webb*, 1986]. Significantly, in a 2CM this can transform a type C3 loop into a type C1 loop, which could otherwise be produced only by a 3CM, if event

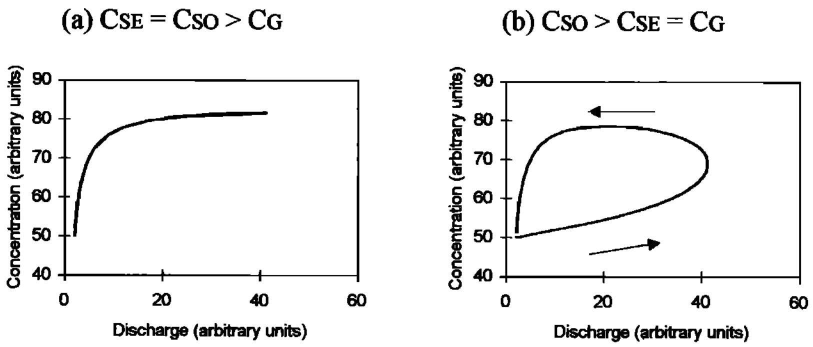

Figure 4. Modelled C/Q loops for which two components have equal concentrations. All component discharges as in Figure 1. (a) $C_{SO} = 150$, $C_{SE} = 150$, and $C_G = 50$. (b) $C_{SO} = 150$, $C_{SE} = 50$, and $C_G = 50$.

water concentrations initially exceed pre-event levels. Given the possibility of flushing, then, a C1 loop cannot be taken as definite evidence for a 3CM. It should be noted in this respect, however, that type A1 hysteresis cannot be generated by a 2CM, even with flushing (as this would imply increasing rather than decreasing event water concentrations). The observation of a type A1 loop for one or more solutes is therefore an important confirmation that a 3CM is in operation.

In a 3CM the impact of flushing will depend on the type of loop normally observed, having most significance where C_{SE} would otherwise be low. In general, hysteresis form will be transformed (with increasing levels of flushing) according to the sequences A1 → A2 → C2 or A3 → C3 → C1. Although problematic for interpretation, flushing should usually be identifiable among a set of C/Q plots. Within a single episode, rising limb C_T peaks for a flushed solute will precede those for normal type C1 or C2 solutes. Additionally, as flushing is most likely after extended dry periods or autumn leaf fall, the occurrence of type C1 or C2 loops for a given solute only at these times may suggest flushing. A solute which exhibits these hysteresis forms throughout the year is probably not affected by this process.

Of the other components in the 3CM, C_{SO} is thought likely to be fairly stable, as equilibrium reactions such as cation and anion exchange minimize temporal variations. It is possible that C_G may decrease during episodes, as weathering reactions may be too slow to offset dilution by infiltrating event water. In this situation postepisode C_T will not return to pre-episode values, giving a readily identifiable "open-ended" loop.

2.6. Analysis of Stream Data

The methods developed for C/Q analysis were applied to ERP data from four streams in the Southwestern Highlands region of the Adirondacks: Bald Mountain Brook, Buck Creek, Fly Pond Outlet, and Seventh Lake Inlet. The first- and second-order streams are located close together and have broadly similar characteristics. All are underlain by Precambrian granitic gneisses and metasediments and covered by sandy glacial till. Soils are Spodosols, and all basins are forested with a hardwood/conifer mixture. Wetlands in low-relief valley areas are believed to generate SOF.

Of five monitored streams in the Pennsylvania region, Linn Run and Benner Run had sufficient monitored episodes for analysis. The second-order, forested basins have not been glaciated and are underlain by sandstone and some shale. Soils are mainly acidic Hapludults and Dystrochrepts. Basins are larger than those in the Adirondacks, and loadings of atmospheric pollutants are higher in this region. Benner Run contains wetland areas close to the stream, while Linn Run has a higher relief and does not contain wetlands. Linn Run is more acidic. Further details of all watersheds are given by *Wigington et al.* [1996].

For analysis, episodes were required to be single-peaked, with at least two samples collected on each limb of the hydrograph, and one at or close to peak discharge. This was considered to be the minimum from which rotational direction could be determined. Identifying curvature often required additional samples, but the exact number varied according to the type of loop and to the times at which samples were collected. The most common limitation was insufficient sampling of the short-duration rising limb. Full classification was undertaken only where curvature could be characterized and where a loop corresponded to one of the modelled forms. In the following section, analysis has carried out for four chemical variables: ANC, Na^+, K^+, and SO_4^{2-}.

Table 2. C/Q Hysteresis Classifications, Summer/Fall Events, Adirondack Streams

Variable	Events	Clockwise	Anticlockwise	No Hysteresis	Dominant Type(s)
ANC	25	24	0	1	C1 (12), C3 (8)
Na^+	25	22	0	3	C3 (19)
K^+	25	20	2	3	C1 (18)
SO_4^-	25	0	25	0	A1 (18)

3. Results

3.1. Adirondack Streams

Spatial differences in results between Adirondack streams are minor, and they are considered as a group. However, there are significant seasonal variations in behavior. C/Q plots for snowmelt episodes tend to be strongly open-ended, probably because of dilution of groundwater by infiltrating meltwater. These episodes are therefore unsuitable for analysis. Spring episodes were generally undersampled, and only six could be analyzed. These showed relatively subdued chemical variation, consistent with the suggestion of *Hooper et al.* [1990] that soil water may dominate runoff during this period because of wet conditions and low-intensity precipitation.

Summer/fall events were better sampled, and C/Q plots conformed well to theoretical models. These were therefore considered in detail. A total of 25 episodes met minimum sample criteria (five to seven per stream), and these were classified as shown in Table 2. Where more than 75% (an arbitrary threshold) of events fit a given category, the number of is highlighted. Figure 5 shows C/Q plots for an intense, 1-hour June thunderstorm at Fly Pond Outlet.

ANC exhibits clockwise hysteresis in 24 out of 25 episodes. All fully classifiable loops are types C1 or C3, both of which suggest that soil water is the most acidic runoff source. The highest ANC component appears to vary between groundwater and surface event water. The C1/C3 split occurs mainly on an interstream basis (six out of eight type C3 loops occur at Buck Creek) and is not thought to be linked to flushing.

Twenty-two out of 25 episodes show clockwise Na^+ hysteresis, of which all 19 classifiable loops are type C3. This implies a highly consistent component ranking of $C_G > C_{SE} > C_{SO}$. K^+ hysteresis is also clockwise in 20 episodes, but a predominantly type C1 classification indicates a component ranking of $C_{SE} > C_G > C_{SO}$. Hysteresis tends to be less pronounced during fall, and two November episodes actually exhibit anticlockwise hysteresis. It is believed that soil water K^+ is depleted during summer but increases to a level comparable to or greater than surface event water in fall.

SO_4^{2-} hysteresis is remarkably consistent, with anticlockwise loops in all 25 summer/fall episodes. Eighteen are classifiable as type A1. From the earlier discussion the observation of this hysteresis type strongly supports the use of a 3CM to interpret observations. The implied component ranking is $C_{SO} > C_G > C_{SE}$.

3.2. Pennsylvania Streams

Eight episodes were suitable for analysis at Benner Run, and 13 at Linn Run. These were fairly well distributed over the year, and strong seasonal variations in results were not evident

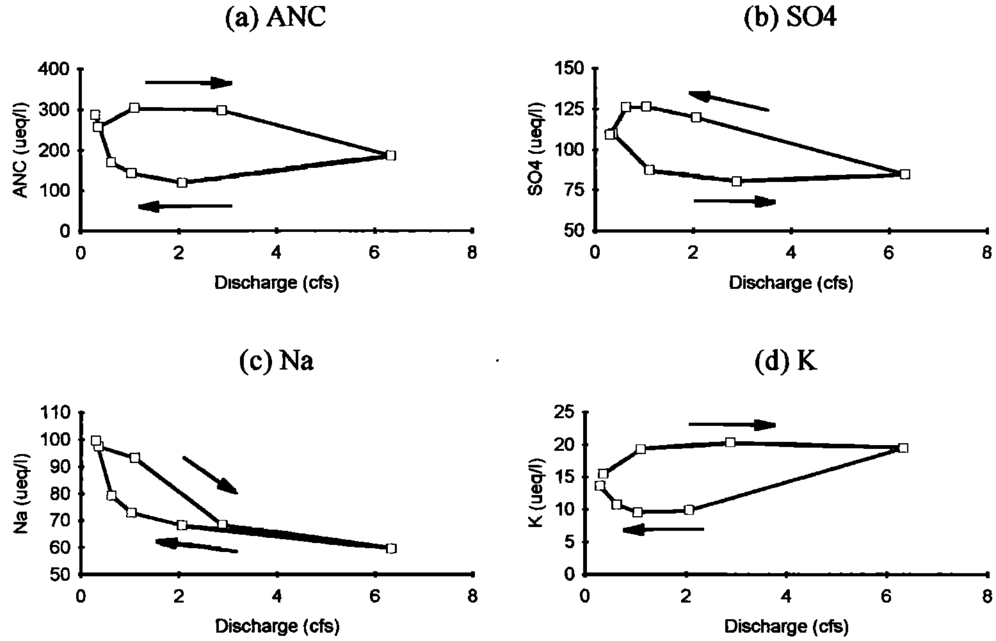

Figure 5. *C/Q* plots for June event, Fly Pond Outlet, Adirondacks.

(partly because snowmelt events did not occur). Classifications for each stream are shown in Tables 3 and 4. *C/Q* plots for a fall event at Benner Run are shown in Figure 6.

For Benner Run, results show a striking similarity to those for the Adirondacks. All events with ANC data show type C1 hysteresis, giving a ranking of $C_{SE} > C_G > C_{SO}$; soil water is again the most acidic flow source. Where observed, Na^+ hysteresis is also clockwise, with a C1 or C3 classification. K^+ exhibits clockwise hysteresis in six episodes, classified as type C1 in five. The $C_{SE} > C_G > C_{SO}$ ranking is the same as that for the Adirondacks. SO_4^{2-} hysteresis is anticlockwise in seven out of eight events, all classifiable as types A2 or A1. Either suggests that soil water has the highest SO_4^{2-}.

Hysteresis at Linn Run is less marked than at Benner Run for most solutes. ANC exhibits C1 or C3 type hysteresis is six episodes, and no clear patterns emerge for Na^+, which is low and fairly invariant at this stream. Type C1 K^+ hysteresis is observed in four episodes, all of which took place in the June–November period. For the remainder of the year, concentrations remain at a low level. SO_4^{2-} is more consistent, with 10 out of 13 episodes showing anticlockwise hysteresis. Six of these can be classed as type A1, suggesting that $C_{SO} > C_G > C_{SE}$.

4. Discussion

Results generally indicate consistent patterns of *C/Q* hysteresis for the solutes analyzed. A number of these patterns are common to streams in both regions, despite differences in geology, soils, topography, and deposition loadings. It is predicted that in the Adirondacks (during summer/fall), surface event water has characteristically high K^+, high to moderate ANC, and low SO_4^{2-}. Groundwater has a fairly similar ANC and high Na^+. Soil water has high SO_4^{2-} and low ANC and Na^+. A comparison can be made between these predictions and previous measurements made at similar locations. The Adirondack studies considered here are those by *Mollitor and Raynal* [1982], *David and Driscoll* [1984], *Cronan* [1985], *Shepard et al.* [1990] and *Foster et al.* [1992]. All studies monitored mineral soil water, and some give values for lakewater or streamwater which are used to represent groundwater. Surface event water was considered potentially to be either unaltered throughfall or to undergo modification at the surface during overland flow. Unfortunately, none of the studies listed sampled overland flow, and it is doubtful that hillslope organic horizon leachate represents a suitable proxy given that SOF is likely to occur in wetland areas.

If it is assumed that throughfall represents surface event water, SO_4^{2-} predictions are in excellent agreement with previous measurements. All studies support the predicted component ranking of $C_{SO} > C_G > C_{SE}$. Similarly, measurements of K^+ indicate as expected that $C_{SE} > C_G > C_{SO}$. K^+ is leached from organic material but tends to be adsorbed in mineral horizons [*Likens et al.*, 1994]. Although throughfall enrichment would be sufficient to explain observed hysteresis, it is consid-

Table 3. *C/Q* Hysteresis Classifications, Full Year, Benner Run

Variable	Events	Clock-wise	Anti-clockwise	No Hysteresis	Dominant Type(s)
ANC	7	7	0	0	C1 (7)
Na^+	7	5	0	2	C1 (2), C3 (2)
K^+	7	6	0	1	C1 (5)
SO_4^{2-}	8	0	7	1	A2 (5), A1 (2)

Table 4. *C/Q* Hysteresis Classifications, Full Year, Linn Run

Variable	Events	Clock-wise	Anti-clockwise	No Hysteresis	Dominant Type(s)
ANC	13	6	1	6	C1 (3), C3 (3)
Na^+	13	2	4	7	none
K^+	13	4	0	9	C1 (4)
SO_4^{2-}	13	1	10	2	A1 (6)

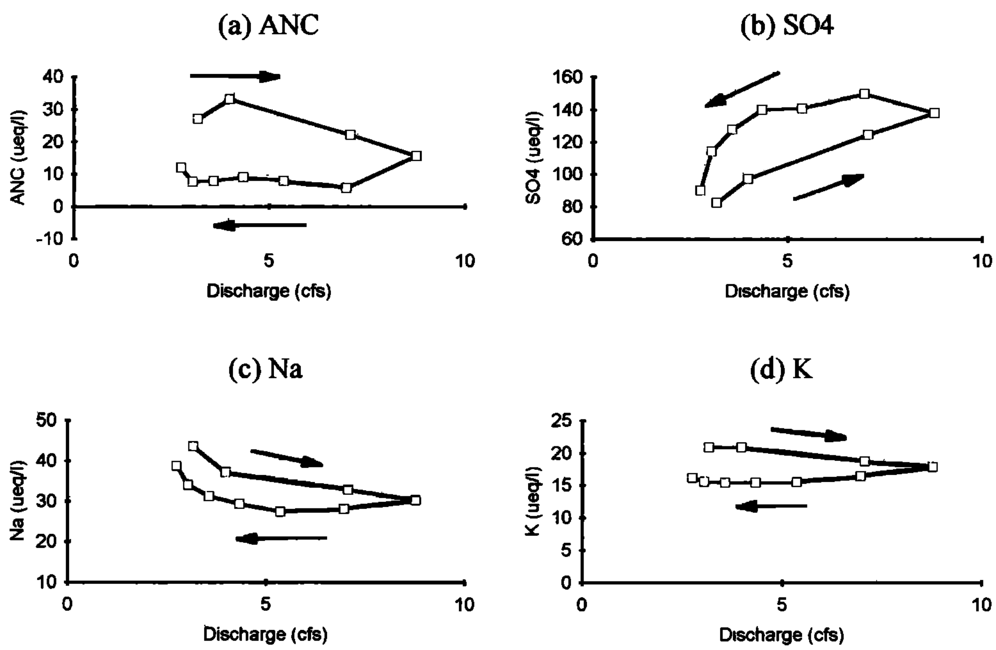

Figure 6. C/Q plots for September event, Benner Run, Pennsylvania.

ered likely that further K^+ is released from the watershed surface. Where overland flow has been sampled, albeit at quite different basins in Amazonia and Queensland, it appears that K^+ increases significantly on contact with the surface [*Elsenbeer et al.*, 1995a, b]. ANC was not measured in any of the previous studies, but an indication can be gained from values given for H^+. As expected, groundwater is relatively alkaline, and soil water is acidic. However, the consistently acidic nature of throughfall appears to be at odds with the high ANC predicted for surface event water from C/Q analyses. It is thought, however, that this discrepancy can be explained by surface interactions, particularly within wetlands. *Hill* [1993] has shown that concentrations of Ca^{2+}, Mg^{2+}, and Na^+ in throughfall can increase by 35–50% within a minute of contacting wetland substrates. This would explain higher than expected ANC in surface event water. Na^+ results are also consistent with this hypothesis; previous studies show high levels in groundwater, but throughfall concentrations are lower than those in soil water. Again, therefore, some surface interaction is necessary to explain observed hysteresis (although not presented here, the same findings are obtained for Ca^{2+} and Mg^{2+}).

Before comparing Pennsylvania results to previous studies, it is useful to examine differences between the two streams, particularly with regard to Na^+ and K^+. At Benner Run, Na^+ is thought to derive from a groundwater brine source. As a result, behavior is similar to that in the Adirondacks, where Na^+ is mainly weathering-derived [*Munson et al.*, 1990; *Evans et al.*, 1996]. At Linn Run there appear to be neither major weathering or brine sources, and Na^+ is consistently low. Contrasts in K^+ hysteresis may be explained by hydrologic differences. At Benner Run, wetland areas generate significant SOF, and interaction with surficial materials produces high surface event water K^+ throughout the year. At Linn Run, without wetlands, surface event water inputs are thought to be limited to direct channel interception [*DeWalle et al.*, 1988a; *Swistock et al.*, 1989]. This will retain a throughfall composition, with K^+ enrichment confined to the growing season. As a result, type C1 hysteresis is observed during this period, but concentrations are uniformly low for the remainder of the year.

Previous measurements in Pennsylvania have been given for Peavine Hill by *DeWalle et al.* [1988b] and for Fish Run (a tributary of Linn Run) by *Swistock et al.* [1989]. Measurements have also been made of shallow soil water, throughfall, and base flow by the first author during fall 1995 at Benner Run (C. Evans et al., manuscript in preparation, 1997). Again, overland flow was not sampled. All three studies, like those for the Adirondacks, support predictions of high SO_4^{2-} in soil water and high K^+ in throughfall. ANC (on the basis of H^+ values) is highest in groundwater but lower than expected in throughfall relative to soil water. Na^+ is also lowest in throughfall, which is inconsistent with the $C_{SE} > C_{SO}$ ranking indicated by clockwise hysteresis at Benner Run. This again suggests that at Benner Run at least, surface event water is modified by contact with the watershed surface.

5. Conclusions

It has been demonstrated that C/Q hysteresis takes on one of a range of characteristic forms depending on the flow system in operation and takes on the ranking of solute concentrations in different components. While, as emphasized by *Christophersen and Hooper* [1992], absolute component concentrations cannot be determined from stream data alone, the methods presented here make it possible to predict relative values based on simple criteria.

C/Q hysteresis observed for the Adirondack and Pennsylvania ERP streams has been interpreted in terms of a 3CM of groundwater, soil water, and surface event water. The hydrologic model used is thought to be realistic in terms of flow generation theories and is consistent with most previous 3CM hydrograph separations. In general, predicted component rankings for a range of solutes agree well with measurements obtained during other studies. This would seem to support the assumptions of the model used, in that an invalid model would not have given realistic results. Those discrepancies which do arise can be explained by base cation release from wetlands during saturation overland flow. It is also apparent that the exact nature of "surface event" water may differ between basins; in the Adirondack streams and Benner Run, it is thought to consist mainly of saturation overland flow, whereas at Linn Run it may be confined largely to direct channel interception.

It is thought that the methods presented here may be applicable to a wider range of basins, although clearly it is essential that a particular basin should conform to the assumptions of the hydrologic model used. The approach should primarily be of use for those studies, such as the ERP, where component compositions have not been quantified. By obtaining chemical signatures for stream components, it may be possible to infer runoff mechanisms and potential sources of chemical modification during transit. These results can provide a basis for future sampling. The approach may also be useful for studies in which components have been identified and sampled, in order to verify that the model proposed is consistent with stream variations for a wide range of solutes, rather than a limited set of tracers.

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