CONCENTRATION/DISCHARGE HYSTERESIS ANALYSIS OF STORM EVENTS AT THE PANOLA MOUNTAIN RESEARCH WATERSHED, GEORGIA, USA

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Abstract. The relationship between discharge and solute concentration was investigated at the Panola Mountain Research Watershed (PMRW), near Atlanta, Georgia, between the water years 1986-2002. Applying previous work by Evans and Davies (1998), the characteristics of the hysteresis loops were used to evaluate the temporal variation of the relative contribution to streamflow of source waters including groundwater (C_G), soil water (C_{SO}), and surface event water (C_{SE}). Twenty-six storm events were evaluated for the concentrations of acid-neutralizing capacity (alkalinity or ANC), pH, specific conductance, SO_4^{-2}, and Cl^-, yielding 116 hysteresis loops.

Concentrations displayed circular hysteresis loops during most storm events, highlighting the complex relation among solutes and discharge during storm hydrographs. In general, the type of hysteresis loop generated by an individual storm and that storm's respective component rankings correlated in a predictable manner. The solutes that have the highest concentrations in groundwater at PMRW include ANC, pH, and Cl^- producing concave, negative trending, clockwise and anti-clockwise loops, indicating a concentration component ranking of $C_G > C_{SE} > C_{SO.}$ In contrast, the solute with highest concentration in throughfall and overland flow was SO_4^{-2} producing positive trending, anti-clockwise hysteresis loops. Specific conductance did not produce a majority of clockwise or anti-clockwise loops; therefore, it could not utilized in the investigation. The analysis of the solute concentration data indicated that groundwater dominates stormflow in PMRW with 67% of events displaying a discharge component ranking of $C_G > C_{SE}$ or C_{SO}, and only 23% of events showed C_{SE} as the largest component.

INTRODUCTION

Within a given watershed, there is a dynamic relationship between discharge and solute concentration during a storm event. This relationship may be represented in a circular pattern that is referred to as hysteresis. The pattern of the relationship between discharge and concentration is circular because the total concentration levels of solutes vary during different periods of a storm. Existing research has demonstrated that the variation in concentration is not merely the product of dilution, but is also caused by "end-member mixing"; that is, the mixing of the different components of discharge, which are quantities of water from multiple sources. This study uses a graphic representation of hysteresis in which measurements of the discharge of a stream during different stages of a storm event are plotted with corresponding concentration levels of dissolved solutes. Applying previous work by Evans and Davies, the characteristics of the hysteresis loops are used to determine which end-member of the discharge, groundwater, soil water, or surface event water, predominates among the three, and in where in the hydrograph it is present in its greatest amount. Different solutes are associated with the sources of different end-members of discharge, and the concentration levels of particular solutes are utilized in developing the hysteresis loops for this study. The solutes measured for this study are: Acid Neutralizing Capacity (ANC), pH, Specific Conductance (SC), sulfate (SO_4^{-2}), and chlorides (Cl^-).

The purpose of this paper is to (1) describe the characteristics of end-member mixing of a small forested watershed using a graphic representation of hysteresis, (2) to explain the mechanisms that control the majority results of the hysteresis loops, and (3) to explain the mechanisms that control those hysteresis loops that deviate from the majority results.

STUDY AREA

The Panola Mountain Research Watershed (PMRW) is a core research watershed under the USGS's Water, Energy, and Biogeochemical Budgets (WEBB) program to study small watersheds in geographically and ecologically diverse regions. PMRW is located about 25 kilometers southeast of Atlanta, Georgia, and is completely contained inside the Georgia Department of Natural Resources, Panola Mountain Conservation Park (Figure 1). Since 1984, hydrological and metrological research has been conducted in the watershed; prior to that date it was used in the Acid Precipitation Thrust Program.

The watershed is 41 hectares (ha) and contains 93% (34ha) forested area that consists of 30% deciduous trees, 32% coniferous trees and 31% mixed deciduous and coniferous forest (Peters, 1994). A 7 ha granite bedrock outcrop, covered by lichen, moss, and small stands of shrubs and trees, makes up the rest of the land use (USGS, 2000). The outcrop is at PMRW's highest elevation, 279 meters ASL, and the watershed has a maximum relief of 55 meters.

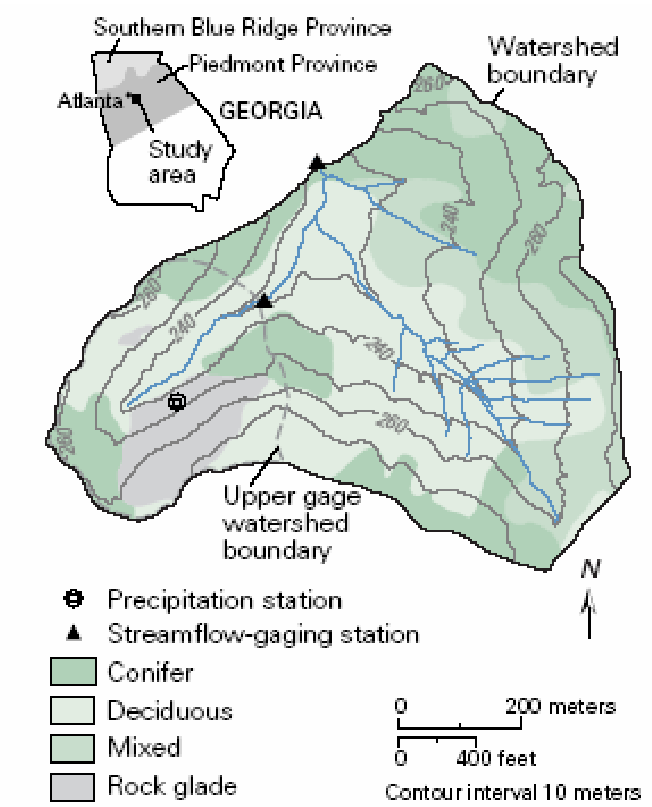

Figure 1. Map of the Panola Mountain Research Watershed (from USGS, 2000).

METHODOLOGY

The data for this study cover a time period of October 1985 through October 2002. There were 65,366 individual discharge measurements made during those years, and all measurements are in the units of liters per second (l/s). The largest measured discharge was 973.41 l/s on July 11, 1994. The water quality data consisted of 3,814 individual measurements at the lower gage. The solute concentrations used for the C/Q hysteresis in this study were Acid Neutralizing Capacity (ANC), Specific Conductance (SC), pH, sulfate (SO_4^{-2}), and chlorides (Cl^-).

The original datasets obtained from the USGS were edited to retrieve discharge data and water quality data from the lower gage. All maximum, minimum, and average values used in this study issued during the water years 1986 through 2002.

A strict criterion was determined to select storm events for analysis with hysteresis loops. The criteria used were that the hydrograph of the event had to have a single peak and had to have a minimum of three water quality measurements on the rising limb and three on the falling limb. All water quality and discharge data were first sorted into their corresponding water years. Initially, the storm events' discharges were to be categorized into a ranking system of the water years' 10^{th}, 50^{th}, and 90^{th} percentile storm events. The storms were sorted under this ranking system, but this approach had to be discontinued because there were not enough corresponding water quality data to establish the hysteresis loops. Because the number of edited discharge measurements outnumbered the water quality measurements by nearly two to one, it was decided to find consistent blocks of water quality measurements and then to assess the corresponding (date and time) discharge data to determine if the storm hydrographs meet the selected criteria. This method identified 58 possible events to be investigated; however, only 26 storm events met the criteria listed above and were selected for plotting of the hysteresis loops. Of the 26 storm events selected, 22 events started at baseflow and four started above the typical level of baseflow.

A criterion to coordinate the time of the solute concentration measurements and the time of the discharge measurements was developed and was used consistently throughout the study. If possible, the exact time of the discharge measurement was coordinated with the solute measurement. If two discharge measurements fell within one minute before and after the solute measurement, only the discharge measurement the minute before was used. If discharge measurements fell beyond one minute before or after, the discharge measurement with the closest time to the solute measurement was used. Discharge measurements, especially during the falling limb of the event, could have a discrepancy of up to 30 minutes due to the automatic samplers going below the threshold of one minute "event" sampling rates.

HYSTERESIS

Stream water concentrations can be dynamic in periods of increased discharge (Evans, *et al.*, 1998). It was previously thought that surface runoff dominated the early storm event on the rising limb, followed by the contribution of soil water, and that ground water dominated the flow on the hygrograph's falling limb. It has been shown that a system can follow the pattern of surface runoff, soil water, and then groundwater dominance, as stated above, but that storm events can be dominated by different sequences of water contributions. Previously, it was thought that as discharge increases, chemical concentrations would decrease. This decrease was believed to be a dilution of the groundwater chemicals by overland surface water. However, more studies have shown that C/Q hysteresis analysis is rarely linear, and that it tends to produce a circular pattern from the differing concentrations on the rising and falling limbs (Walling and Webb, 1986). This circular pattern is called a C/Q hysteresis loop.

Analysis of component mixing and C/Q hysteresis analysis can be studied with a two component end-member system (2CM) or three component end-member system (3CM). In a 2CM system two end members, "pre-event" and "event" ($C_{PRE\text{-}EVENT}$ and C_{EVENT}) water, are considered. Pre-event water is usually groundwater, which is considered to be chemically and isotopically conservative and makes up the contribution of streamwater at baseflow (Evans and Davies, 1998). At this stage, the total concentration is said to be equal to the concentration of groundwater (C_T=C_G). Event water is typically in the form of precipitation or throughfall. *Evans and Davies* (1998) explain that in systems where soil zone water makes a significant contribution and is chemically or isotopically distinct, three end members should be used: groundwater (C_G), soil water (C_{SO}) and surface event water (C_{SE}). In this case a three component mixing model is used: (C_T=C_G+C_{SO}+C_{SE}).

If hysteresis loops are observed that are clockwise or anti-clockwise and convex, or if the hysteresis loops deviate from a linear mixing line, a need for a third component is implied (Evans and Davies, 1998). Because all of the C/Q hysteresis loops in this study are not linear, a 3CM model is used. Table 1 describes all the component rankings for 3CM, as mentioned above, as well as for 2CM models.

Table 1. Diagnostic Features Used to Determine Component Ranking (from Evans and Davies, 1998).

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	$C_G > C_{SO} > C_{SE}$	$C_{PRE\text{-}EVENT} > C_{EVENT}$

DISCUSSION

In this study, 26 storm events were plotted, yielding 116 hysteresis loops. The concentrations measured were ANC, pH, Specific Conductance (SC), SO_4^{-2}, and Cl^-. The majority of the storm events produced hysteresis loops in a circular pattern, highlighting the complex behaviors of solutes and discharge in different portions of a storm's hydrograph. In general, the type of hysteresis loop generated by an individual storm and that storm's respective component rankings correlated in a predictable manner. The solutes that would be expected in the groundwater systems at PMRW produced clockwise loops, indicating a concentration component ranking of C_G>C_{SE}>C_{SO}. Conversely, solutes assumed to come from throughfall and overland flow produce anti-clockwise hysteresis loops. The analysis of the data, based on a majority of storm events during the water years 1986-2002, indicated that groundwater is the dominant water in the storms' total discharge in respect to concentration levels. In the total C/Q analysis, 67% of events displayed discharge component rankings of C_G>C_{SE} or C_{SO}, and only 24% of events showed C_{SE} as the largest component. The other

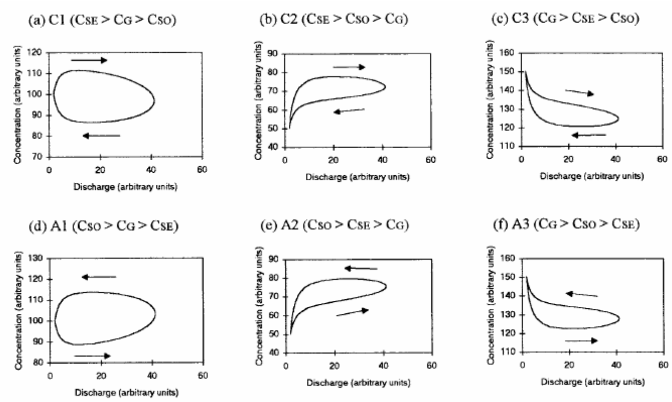

Figure 2. C/Q Hysteresis episodic behavior (from Evans, et al. 1998).

9% of events generated C/Q loops that did not conform to the six hysteresis loop models used for this study and as presented by Evans and Davies.

In the C/Q analysis of ANC and pH, the dominant hysteresis loop type was C3 (39 of 50). As stated above, this is an expected result; because ANC uses the dissolved solids to neutralize acids, and these solids have their highest concentrations in baseflow, which is assumed to be the groundwater component, it is expected that the highest concentration will be on the rising limb and fall to a lower concentration as the event component overtakes the groundwater on the falling limb. Hysteresis of pH is similar; the pH of groundwater is more neutral than the event water components, and pH will have its highest concentration on the rising limb, followed by a clockwise fall as the more acidic event water enters the streamwater on the falling limb.

The hysteretic analysis of SO_4^{-2} produced a dominant loop type of A2 (19 of 25), showing that the total concentration level was at its maximum on the falling limb of the events. This loop type indicates that the soil water component is the largest, followed by the surface event and groundwater ($C_{SO}>C_{SE}>C_G$). The positive trend indicates that the C_T is consistently higher during the event at baseflow (Evans and Davies, 1998). The low SO_4^{-2} concentration in groundwater at PMRW has been attributed to the soil's ability to retain SO_4^{-2} and to increase the concentration of soil water as a result of its mobilization in the surface, organic-rich, soil horizons (Peters, 1994). As stated above, this would be an expected result, given that there are no known sources of SO_4^{-2} weathering from the local strata, and all SO_4^{-2} is assumed to be atmospherically deposited. The most likely route for sulfate transport is runoff from the 7ha granite outcrop and through direct input into the soil. In previous studies it has been noted that the SO_4^{-2} concentrations were higher in the runoff from the outcrop than in the corresponding precipitation, because the rainwater releases the SO_4^{-2} that has been dry-deposited on the exposed bedrock (Peters, 1994).

The C/Q analysis of specific conductance did not produce any dominant loop types, therefore, could not be used to contribute to the analysis.

Categorizing these events by amount of precipitation in the specific event, season, or above and below average precipitation did not result in any pattern that would suggest that any of these variables were controlling the concentration levels that produced the different style loops. However, when these events were compared to their corresponding antecedent precipitation index (API) values, storms with API values higher than 50 tended to produce clockwise loops and storms with API below 36 tended to produce anti-clockwise loops. Nonetheless, two events at high API values, 82 and 121, also produced an anti-clockwise loop. The comparison of hysteresis loops with API values indicates that events with moderate to high APIs possibly have low concentrations of total dissolved solids (TDS) in the soil water and runoff because the bedrock has already been "washed" of its TDSs and, additionally, the soil also has been flushed by previous events. When this event water is added to the groundwater component of the hydrograph, it dilutes the solids present in the groundwater and produces a clockwise C3 hysteresis loop. Conversely, in events with low API values, the soil would have low moisture content and could therefore be assumed to have retained solids from previous events, and then event water transports these solids to the stream during the subsequent rain events. This contribution from soil water would peak on the falling limb of the storm (groundwater will always have the highest concentration of TDS because it is supplied as a weathering product from the strata) and produce an anti-clockwise A3 loop.

Chloride C/Q analysis did produce a majority of clockwise C3 loops (14 out of 25); however, eight events were anti-clockwise (5 A3 and 3 A2). Since the Cl^- is deposited from rainfall in the watershed, and is extremely mobile and very soluble, it is expected that the groundwater component would have the highest concentration of Cl^- (Berner, 1986). Although there are differences in the rotational directions of the various loops, the chloride loops are all concave and have a negative trend (19 of 25). This confirms that groundwater has the largest concentration at the beginning and ending of the event. As in the SC analysis, the anti-clockwise deviation from the majority could not be categorized by season or precipitation; one explanation could be justified when these events are compared to the amount of annual runoff at PMRW.

Events that occurred within water years of higher than average runoff produced the majority of the anti-clockwise loops describing Cl^- concentration (7 of 8). This again is expected, due to the proportionality of increased precipitation to the amount of Cl^- being deposited in the watershed. However, within the two types of anti-clockwise loops (5 A3 and 3 A2), comparisons of the events' loops with corresponding API values suggest that events with moderate API values (32 through 36) have concentrations consistent with a larger groundwater component (A3), while events with larger API values (>42) have concentrations consistent with a larger soil water component (A2).

Although most of the concentrations used in the C/Q analysis emerged with a specific type of episodic behavior, attention should be paid to the mechanisms that possibly control those events that deviate from the majority. In the analysis of storm events with discharge levels that rated the event as the 99^{th} percentile storm for its respective water year, a change from the expected form occurred. Prior to these events, the measured concentrations of ANC, pH, SC, and Cl^- generally produced a majority of clockwise loops. However, during these 99^{th} percentile storms, all C/Q analysis produced anti-clockwise loops of the A3 type, $C_G>C_{SO}>C_{SE}$, which indicates that the groundwater component does not become dominant until the falling limb of the storm. This is most likely due to the intensity of the event water diluting the TDSs that are incorporated in the soil water and runoff. The lack of TDS in the soil diminishes its ability to neutralize the precipitation until the lagging groundwater component arrives.

In the C/Q hysteresis plot analysis, 12 of the 116 loops did not indicate a specific type of episodic behavior. In four of these events the hydrograph did not start from baseflow, which could have affected the C/Q plot. Further investigation into the mechanisms controlling these C/Q plots is warranted, and will possibly be a future addition to this paper.

CONCLUSION

Concentrations displayed circular hysteresis loops during most storm events, highlighting the complex relation among solutes and discharge during storm hydrographs. In general, the type of hysteresis loop generated by an individual storm and that storm's respective component rankings correlated in a predictable manner.

The solutes that have the highest concentrations in groundwater at PMRW include ANC, pH, and Cl^- producing concave, negative trending, clockwise and anti-clockwise loops, indicating a concentration component ranking of $C_G > C_{SE} > C_{SO.}$ In contrast, the solute with highest concentration in throughfall and overland flow was SO_4^{-2} producing positive trending, anti-clockwise hysteresis loops. Specific conductance did not produce a majority of clockwise or anti-clockwise loops; therefore, it could not utilized in the investigation. The analysis of the solute concentration data indicated that groundwater dominates stormflow in PMRW with 67% of events displaying a discharge component ranking of $C_G > C_{SE}$ or C_{SO}, and only 23% of events showed C_{SE} as the largest component.

It has been shown that the behavior of end-member mixing can be predicted with C/Q hysteresis analysis. At PMRW, 116 hysteresis loops were generated using discharge and dissolved solute measurements over the water years 1986 through 2002.

The episodic behavior of the dissolved solutes measured was consistent and predictable using the solutes that were picked for this study. This predictability is evidence that the 3CM end-member model is accurate.

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