DETERMINING WATERSHED FLOW PATHWAYS USING GEOCHEMISTRY AND TIMING

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Abstract. Investigating storm runoff generation in watersheds is an area of ongoing hydrologic research. Geochemical tracer studies, such as static end-member mixing analysis (EMMA) and hysteresis loop analysis, have been used to evaluate these processes. While EMMA can assess the relative input of flow pathways for individual stream water quality samples collected during a storm, it cannot quantify their contributions continuously. Hysteresis loops of stream discharge versus geochemical tracer concentration can be used to estimate relative inputs of basic end-member pathways, but this approach only suggests the timing and dominance of flow pathways and these patterns alone cannot quantify their contributions.

We propose a new method that incorporates both hysteresis loops and geochemical tracer studies to quantify runoff contributions from watershed flow pathways during a storm. The approach involves estimating relative tracer concentrations of four end-members, along with estimating the percentage of total stream discharge from each end-member. The method has been applied to a 22 year dataset from Panola Mountain Research Watershed, Georgia and has identified two distinct watershed responses to rain events. The responses appear be related to a threshold of 50-60mm of total rain.

INTRODUCTION

Numerous hydrochemical studies have been conducted to investigate the contributions of watershed flow pathways during rainstorms. While this research has identified that pre-event water dominates stream flow during a storm (Pinder and Jones 1969; Sklash and Farvolden 1979; Sklash 1990), it has not been able to determine the actual flow mechanisms or their timings (Buttle 1994). Understanding these processes is important from a watershed management perspective, since the areas of the watershed that generate flow has implications for both flood control and stream ecological health.

Hydrograph separations have been used to divide a storm hydrograph into event (new) and pre-event (old) waters (Pinder and Jones 1969). Pre-event water has been further divided into base flow and soil water (Kennedy *et al*. 1986; DeWalle *et al*. 1988a). This method can provide insight into the timing and source of inputs to stream discharge and the amount contributed from these sources.

One method used to generate hydrograph separations is end-member mixing analysis (EMMA) (Christopherson *et al*. 1990; Hooper *et al*. 1990; Burns *et al.* 2001). EMMA assumes that stream water is made up of a mixture of waters supplied by distinct components of the watershed, each with distinct concentrations of natural geochemicals (Figure 1). The geochemistry can be used to trace the contributions of these watershed components to total stream flow. One drawback of EMMA is that it uses a fixed end-member composition, which likely varies over time. This may lead to results that do not accurately represent the flow contributions of each component during a storm (Hooper 2001).

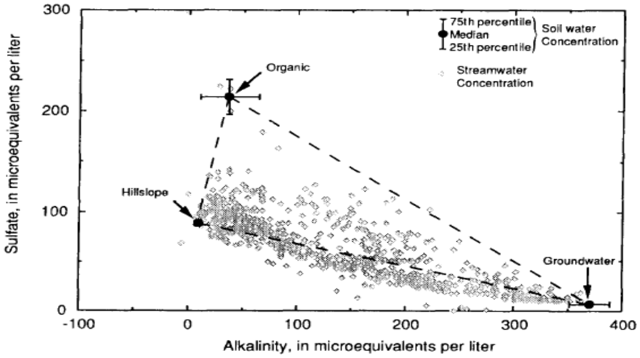


Figure 1. Example of EMMA (Hooper *et al*. 1990).

Another method used to investigate storm runoff generation processes is hysteresis loop analysis (Evans and Davies 1998; Chanat *et al*. 2002). This technique uses the temporal variations in stream tracer concentrations with respect to stream discharge along with approximate tracer concentrations supplied by each component to show hysteresis between the rising and falling limbs of the hydrograph. The hysteresis loop is then matched to a hysteresis loop taxonomy (Figure 2), indicating which component of the watershed dominates flow contributions during a storm hydrograph. This method also has limitations, mainly that it cannot quantify the percentage of contribution coming from each component, and that it cannot provide the tracer concentration of each end-member.

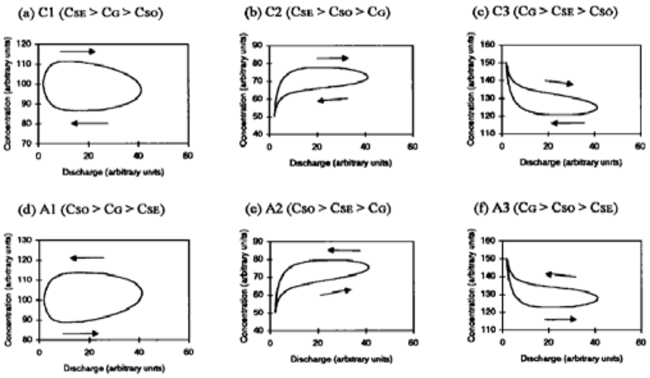


Figure 2. Example of hysteresis loop taxonomy from Evans and Davies (1998).

In this paper, we propose a new method that incorporates elements of both EMMA and hysteresis loop analysis using data collected at Panola Mountain Research Watershed (PMRW). The method uses a range of known end-member tracer concentration values from each watershed component along with estimates of flow pathway contributions and their timing to fit actual hysteresis loops for two natural geochemical tracers. By analyzing the hydrograph separations generated from this method, we can investigate the flow pathways operating in the watershed.

Site Description. PMRW is located approximately 25 km southeast of Atlanta, GA in the Panola Mountain State Conservation Park (Figure 3). The catchment covers 41 ha, of which 90% are covered by forest, with the remaining 10% consisting of exposed granite outcrops (Peters *et al.* 2003). Bedrock at the site is composed mainly of Panola Granite, which is a biotite-oligoclase-quartz, microcline granodiorite along with some scattered pods of amphibolitic gneiss (Higgins *et al*. 1988). Hillslopes comprise most of the catchment (>75%) and have shallow soils (<1 m). The riparian zone, which has the deepest soils (5 m) is relatively narrow (<50 m) and occupies less than 15% of the total catchment area (Peters *et al.* 2003).

Located in the southern Piedmont physiographic region, PMRW has a humid, subtropical climate, with average annual temperature of 16.3°C. Average annual precipitation is 1,220 mm, of which 70% is evapotranspired (Peters *et al.* 2003). Stream discharge fluctuates seasonally, generally with highest baseflows during the November-March dormant season and low baseflows during the May-October growing season (Peters *et al.* 2003; Tromp-van Meerveld *et al.* 2007).

METHODS

Data Collection. The analysis herein uses data collected from PMRW during a 23-year period from October 1985 through September 2008, water years 1986 through 2008. Of the numerous wells and lysimeters present at PMRW, data from 13 groundwater (GW) wells installed at varying depths throughout the watershed was used, along with soil water data from four zero-tension lysimeters (Figure 3). Samples from these sites were collected weekly during the periods when sampling occurred. Precipitation was recorded using tipping bucket rain gages. Wet/dry collectors were used to collect chemistry samples from two throughfall and two precipitation sites (Peters and Ratcliff 1998). Stream stage was recorded at 5 minute intervals during baseflow conditions and at 1 minute intervals during storms in a compound 90° V-notch weir, located at the mouth of the 41-ha watershed. An automatic sampler collected streamwater samples in the weir during rainstorms (Peters 1994). All water samples were analyzed for chloride (Cl^-) and silica (H_4SiO_4) using ion chromatography and either direct coupled plasma or inductively coupled plasma emission spectroscopy, respectively.

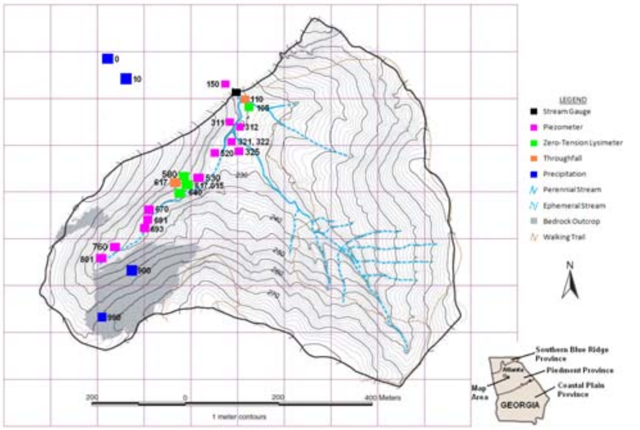


Figure 3. Map of Panola Mountain Research Watershed (PMRW) showing location of sampling sites used in this study.

Data Analysis. Over the 23 year sampling period at PMRW, the start and end times of 139 storms were identified. Of those storms, 39 with single peak hydrographs were used in this analysis.

Chloride and silica were selected as tracers for this study because they behave relatively conservatively at PMRW (Peters and Ratcliffe 1998; Burns *et al.* 2003). At PMRW, chloride concentrations in precipitation are typically low compared to soil water and groundwater, which have relatively similar concentrations. Silica concentrations are extremely low in precipitation, but increase as water has more contact with weathering minerals; the longer water has contact with minerals in the watershed, the higher the silica concentration (Burns *et al.* 2003).

Chloride and silica concentration data from selected sites were plotted on a bivariate graph (Figure 4). Four distinct populations are noted: deep groundwater, shallow groundwater, hillslope 1 water, and hillslope 2 water.

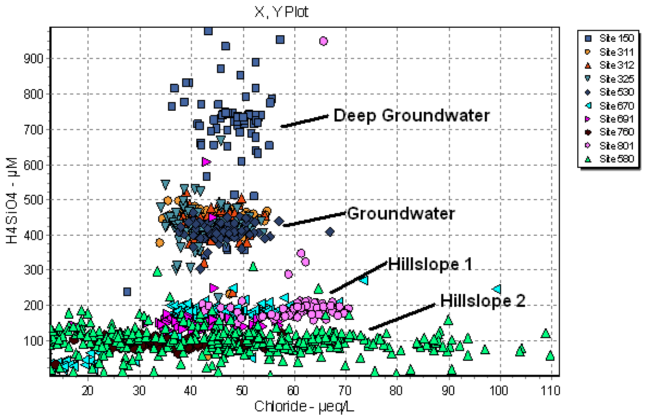


Figure 4. Chloride versus silica concentrations for selected sample sites.

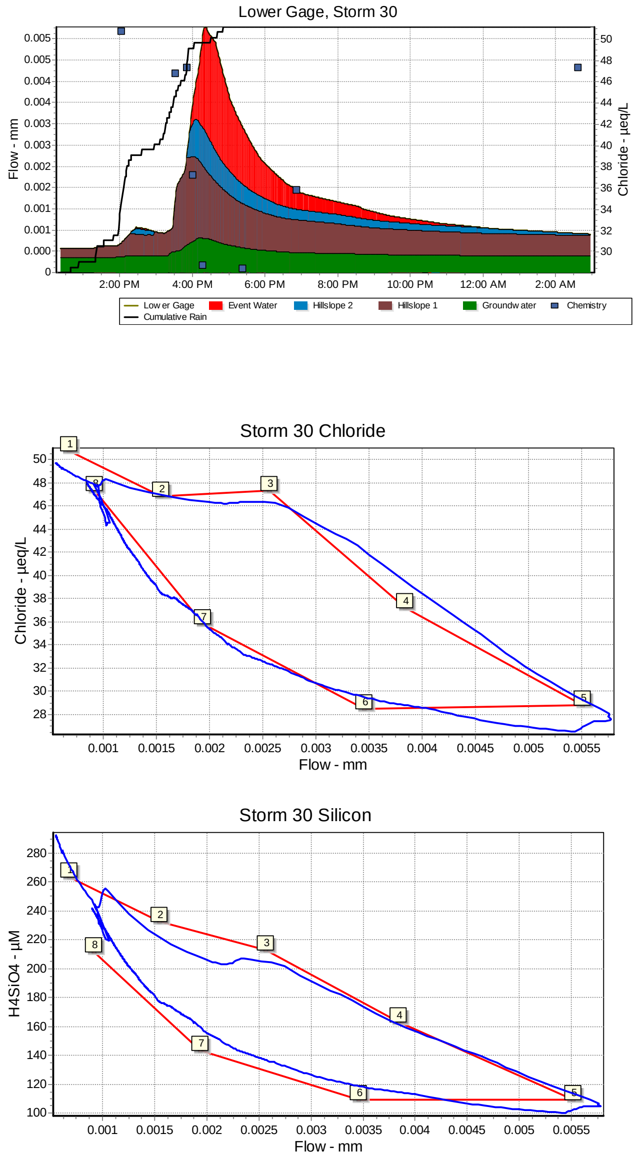
Deep groundwater flowing through fractured bedrock would have to flow through the weathered bedrock/saprolite to reach the stream channel, causing the deep groundwater to mix with the shallow groundwater and become diluted that is with respect to weathering products. Additionally, stream silica concentrations never reach values approaching those of the deep groundwater, indicating that deep groundwater is not a significant contributor to stream flow. Therefore, deep groundwater was not used as a flow component in the analysis. Event water, which consists of runoff from the bedrock outcrop, direct precipitation onto the stream channel, and runoff from variable source areas, was used as the fourth end-member.

The storm hydrograph is subdivided into the four hydrograph components using assumptions about how these components should behave (Figure 5.c). End-member concentrations are used with these components to construct synthetic chemical concentrations using a four component mixing model:

$$C_S Q_S = C_{GW} Q_{GW} + C_{H1} Q_{H1} + C_{H2} Q_{H2} + C_{EW} Q_{EW}$$

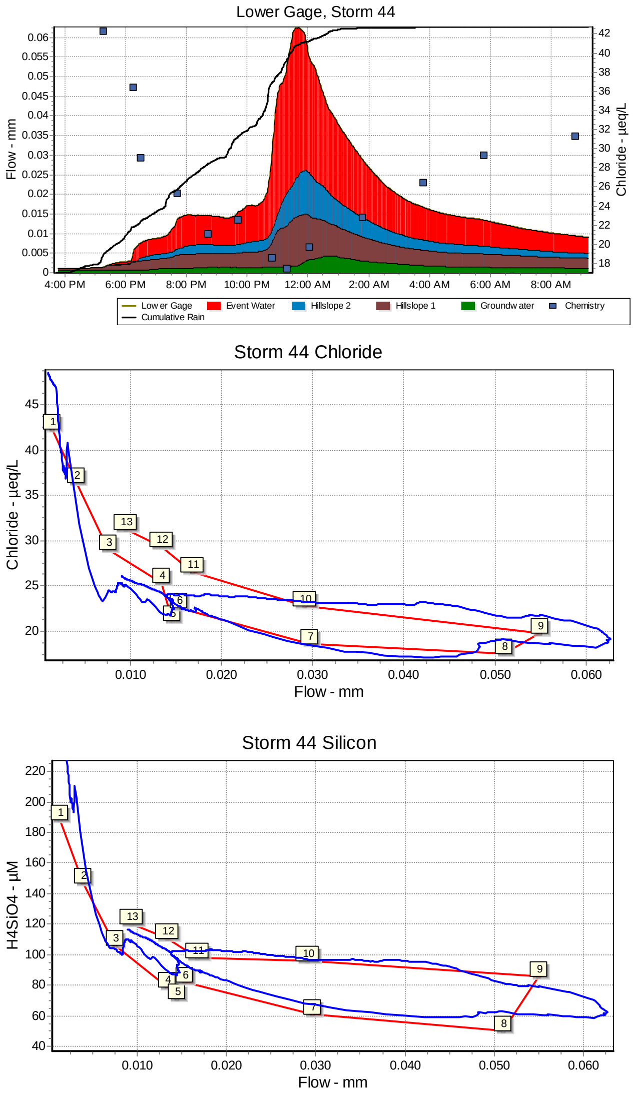
where C is concentration, Q is discharge, S is stream water, GW is shallow groundwater, H1 is hillslope water 1, H2 is hillslope water 2, and EW is event water.

The results of the mixing model are plotted versus the total discharge to construct a synthetic hysteresis loop (Figure 5a, 5b). This loop is compared to the actual hysteresis loop, and the hydrograph components and end-member concentrations are adjusted to achieve a “best” fit. An example of the final fit for Storm 30 during December 10, 1993 is shown in Figure 5.



	Chloride End-member (µeq/L)	Silica End-member (µM)	Runoff Percent
Groundwater	55	375	27.3
Hillslope 1	44	149	44.1
Hillslope 2	28	68	11.5
Event Water	9	2	19.5

Figure 5. Analysis of a rainstorm on December 10, 1993, including (a) hydrograph separation, (b) chloride hysteresis loops, (c) silica hysteresis loops, and (d) table of end-member concentrations and component contributions. In figures b and c, the numbered squares represent sample number in chronological order and the blue line represents the synthetic hysteresis loop.



	Chloride End-member (µeq/L)	Silica End-member (µM)	Runoff Percent
Groundwater	51	375	8.9
Hillslope 1	45	149	23.0
Hillslope 2	34	68	15.5
Event Water	5	2	52.6

Figure 6. Anlaysis of a storm on February 10, 1995, including (a) hydrograph separation, (b) chloride hysteresis loops, (c) silica hysteresis loops, and (d) table of end-member concentrations and component contributions. In Figures b and c, the numbered squares represent sample number in chronological order and the blue line shows the synthetic hysteresis loop.

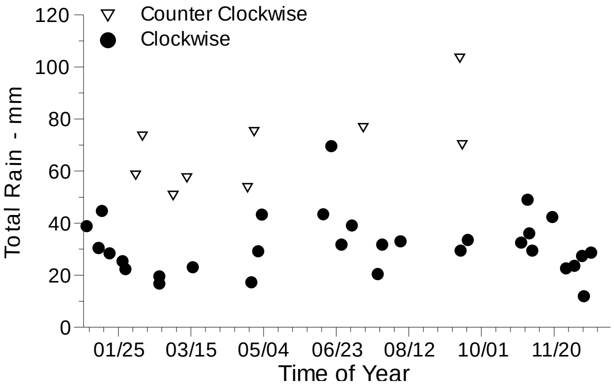


Figure 7. Total rainfall for 39 storms at PMRW. Storms occurred over a 22 year period.

RESULTS AND DISCUSSION

The initial analysis focused on storms with single peak hydrographs and revealed at least two different flow generation patterns occurring in the catchment. Generally, storms behave similarly to Storm 30, with clockwise hysteresis loops for chloride and silica (Figure 5). Tracer concentrations for these storms decrease relatively slowly during the rising limb of the hydrograph, followed by a gradual increase on the falling limb. In order to create an estimated hysteresis loop that fits the observed values, the timing of flow contributions for the pre-event components must be adjusted to occur during the rising limb of the hydrograph. This timing closely matches that of precipitation. Additionally, runoff generated by these storms is dominated by pre-event water.

Although the hysteresis for most rainstorms is clockwise, the hysteresis for a few rainstorms is counter-clockwise, as seen for Storm 44 (Figure 6). It was initially thought that these rainstorms might have a large amount of tracer-dilute water supplied to the stream early during the rainstorm, rapidly decreasing the overall tracer concentration in the stream and thus causing the counter-clockwisehysteresis loop. Analysis of total rainfall (Figure 7), indicates that this is not the case, and that there is a threshold value ranging from 50-60mm of total rainfall that causes the counter-clockwise hysteresis loops. This threshold value matches the threshold value previously noted of 55 mm of rain required to generate significant subsurface flow at a trench in the upper part of PMRW (Tromp-van Meerveld 2006). This suggests that during high volume storms, an additional source of water with a high tracer concentration becomes hydrologically connected to the stream.

CONCLUSIONS

Estimated hysteresis loops of end-member contributions to storm flow have been used to investigate storm runoff generation processes at Panola Mountain Research

Watershed. Analysis of 39 single peak hydrographs has identified at least two flow generation patterns occur with different timing and contributions from the four watershed components. Initial results indicate that a threshold of 50mm of total rainfall is related to these two patterns, where storms that have a total rainfall of less than 50mm have clockwise hysteresis for tracer concentration and storms that reach 50mm or more of total rainfall have counter-clockwise hysteresis.

Future research will focus on using additional tracers in the hysteresis analysis to improve accuracy of the hydrograph separations. We will also investigate the antecedent wetness and additional storm characteristics, with the intent of identifying the mechanisms that generate runoff from each component. More complex multi-peak hydrographs will also be investigated.

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