USING WATER CHEMISTRY DATA TO QUANTIFY SOURCE CONTRIBUTION TO STREAM FLOW IN A COASTAL PLAIN WATERSHED

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Abstract. Dynamics of groundwater recharge in lowland watersheds is not well understood. We studied groundwater recharge and its relationship to stream flow in a 9.86 km^2 catchment within a third-order, 70 km^2 forested watershed in the Atlantic coastal plain of the United States. The objective was to delineate the different sources and contributions of stream flow of upper Turkey Creek, a small, ephemeral blackwater stream in a forested area near Charleston, South Carolina. Our methods included the collection of precipitation and stream water, and also discrete-depth groundwater samples from water table wells and piezometers installed in transects orthogonal to and along the stream channel. Time series water level and water chemistry data showed clear signals due to seasonal climate trends, individual storm events, and daily evapotranspiration forcing. Concentrations of natural chemical tracers (Na^+, Ca^{2+}, Si, Cl^-), as well as water quality indicators (pH, temperature, specific conductance) correlated to fluctuating water table levels in the stream. End-member mixing analysis of water chemistry data indicated that precipitation, water from the hyporheic zone of the stream (upper meter of streambed sediment), and shallow groundwater played a significant role in stream discharge during wet conditions. During dry conditions, precipitation, soil water, and hyporheic zone water were the most important contributors to stream flow. Deeper groundwater seemed to play a relatively minor role to stream flow in this watershed. We have used principal components analysis (PCA) to analyze source and stream data, which to date confirms that antecedent moisture condition in the watershed plays a large role in determining which potential sources may be contributors to stream flow. Ultimately, this work will aid in the development of a geochemically constrained groundwater-surface water model for lowland watersheds for this and similar regions that are under increasing threat from burgeoning population, associated land-use change, and resulting changes to the water budget.

INTRODUCTION

Over the past several decades, population growth has occurred at a rapid rate within coastal communities of the southeastern U.S., much of this growth accompanied by land use change and development. In Charleston, South Carolina, urban land use has increased by 256% between 1973 and 1994 and is predicted to increase by another 200% by 2030 (Allen and Lu, 2003). Numerous studies have linked urbanization to a significant alteration of the hydrologic processes governing watersheds (e.g. Wahl et al., 1997; Watts and Hawk, 2003; Poff et al., 2006), changes which ultimately threaten the quality and health of nearby fresh and estuarine water bodies (Line et al., 1998; Holland et al., 2003; Farahmand et al., 2007).

Lowland watersheds of the southeastern United States are often dominated by wetlands dependent on groundwater discharge and recharge processes (Mitsch and Gosselink, 2000). These complex groundwater and surface water interactions may result in lowland watershed hydrology that is extremely susceptible to the impact of land use change. Until recently, very few long-term studies have focused on the hydrologic processes unique to lowland watersheds of the southeastern, coastal plain. It is important to understand how these watersheds function in their natural state, how they may be impacted by urbanization and to develop a means of minimizing these impacts on surrounding ecosystems.

To study the influence of various sources of water on stream flow, research has relied on the use of chemical hydrograph separation techniques. End-member mixing analysis, a type of chemical hydrograph separation, has been successfully used to incorporate multiple tracers and end-members into source contribution estimates (Christophersen and Hooper, 1992; Mulholland, 1993; Burns et al., 2001, James et al., 2006).

The objective of this study was to delineate the different sources and contributions to the stream flow of upper Turkey Creek, a small, ephemeral blackwater stream in a forested watershed in the Santee Experimental Forest near Charleston, South Carolina.

METHODS

Site Description

The Turkey Creek watershed, or WS-78, is located approximately 70 km northeast of Charleston, South Carolina (Figure 1). The watershed is part of the Francis Marion National Forest and adjacent to the US Forest Service's Santee Experimental Forest, a research forest demarcated in 1936 and managed by the Center for Forested Wetlands Research in Cordesville, SC. WS-78 is managed by the U.S. Department of Agriculture-Forest Service (USFS) for periodic prescribed fire and thinning to control vegetative growth. Elevation of the approximately 70 km^2 watershed ranges between 3 to 15 m above sea level. Land cover within WS-78 is comprised of 40% pine forest, 35% thinned forest, 17% forested wetlands, 5% mixed forest and 3% developed as agricultural lands, roads and open areas (Amatya and Trettin, 2007; La Torre Torres, 2008). Soils are mostly of the poorly-drained, clayey Lenior and Lynchburg series with other interspersed sandy and loamy soils as well as the Meggett series. Meggett series soils are typically developed in riparian corridors and are described as clay-rich in the upper part of the column with sub-soils that are sandy loams (NRCS, 2010). Because of the large size of WS-78, this study focused on a smaller, 986 ha headwaters catchment which has been defined as the Upper Turkey Creek (UTC) subwatershed (Figure 1).

A series of nested piezometers, water tables wells, and stilling wells were installed at UTC by researchers from the College of Charleston and the USFS. The location of piezometers and wells was chosen to monitor groundwater changes over time in a variety of locations in the subwatershed including uplands, upland-wetland transition areas, riparian wetlands, and in stream beds. Also installed at UTC were a series of suction lysimeters in the riparian corridor and uplands, a manual rain gauge in the uplands, and an automated sampler (HACH Co., Loveland, CO) in the stream bed.

Field and Laboratory Data Collection

Hydrologic monitoring and sample collection for this study took place between May 2008 and December 2009.

Groundwater levels were monitored in the water table wells and piezometers on either hourly or four-hourly intervals. Monitoring period was dependent on depth of piezometer or well and location. Stilling wells installed in the stream bed were used to monitor stream stage at 15-minute interval and discharge calculated using the Cipoletti formula (Dingman, 1994). Though a

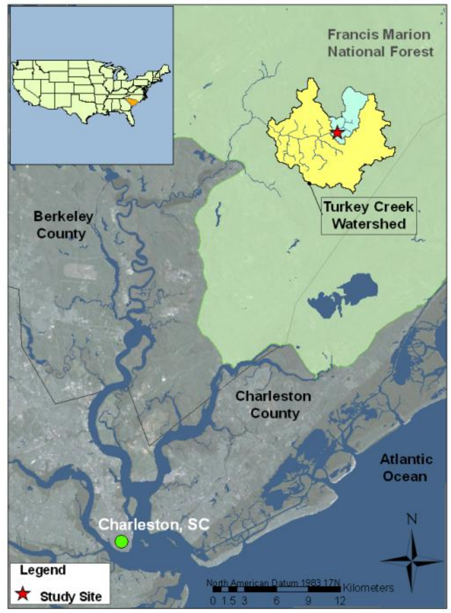

Figure 1. Location map of Turkey Creek watershed in the Francis Marion National Forest. The study site (starred location) is near the outlet of the wetland-dominated headwaters 986-ha catchment of Turkey Creek. The 7,000-ha Turkey Creek watershed is part of the US Geological Stream Gaging network (USGS gage 02172035).

weir to measure flow was not established at UTC, the Cipoletti formula was used to examine generalized stream flow and runoff trends during storm events.

Precipitation was also monitored with a tipping bucket rain-gauge operated by the USFS at UTC.

Sampling for water chemistry analysis occurred regularly on a monthly basis or around storm events between May 2008 and December 2009. Groundwater samples were collected from all piezometers and water table wells with a peristaltic pump or a rotary pump with foot valve. Stream samples were collected using an automated sampler at the stream. Sample collection occurred at either a twenty-four hour interval or adjusted to a four or six hour interval when significant storm events were predicted for the area. Evaporation rate in the automatic sampler was monitored in order to correct tracer concentrations influenced by evaporation during the collection period. Biological and chemical transformations were accounted for in later solute selection in end-member mixing analysis. Only those solutes known to experience no known biological or chemical transformations after collection were incorporated.

Precipitation was collected using a manual rain gauge at UTC and soil water samples were collected using suction-lysimeters installed in the riparian corridor.

Following collection, samples were analyzed for major anions (SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-, F^-, Br^-, PO_4^{3-}) and cations (Na^+, Ca^{2+}, Si, Mg^{2+}, K^+, Fe, Mn) in the laboratory using an ion chromatograph, an inductively-coupled plasma/mass spectrometer, and a total organic carbon analyzer.

End-Member Mixing Analysis

End-member mixing analysis (EMMA) for both watersheds was performed as described by Christopherson et al. (1990), Christopherson and Hooper (1992), and Burns et al. (2001).

A stream water data set, comprised of 250 stream samples, was compiled for the time frame from May 2008 to December 2009. A data set of possible end-members to stream flow was also compiled. End-member water chemistry was represented by the median concentration of each solute over the entire study period.

To incorporate multiple tracers into EMMA and hydrograph separation, principal components analysis (PCA) was used. Stream data was standardized and PCA performed to find a series of principal components that best explained the variability in the entire data set. Steam and source data were then projected into a new *U*-space whose coordinates were defined by the identified principal components. The likelihood for a series of sources to contribute to stream flow was evaluated by examining their ability to encompass all of the stream data in the *U*-space.

PCA was also incorporated into the mixing equations for hydrograph separation. A series of linear equations were solved simultaneously and are described by Burns et al. (2001) as,

$$\begin{aligned} Q_s &= Q_1 + Q_2 + Q_3 \\ U1Q_s &= U1_1 Q_1 + U1_2 Q_2 + U1_3 Q_3 \\ U2Q_s &= U2_1 Q_1 + U2_2 Q_2 + U2_3 Q_3 \end{aligned} \quad (1)$$

where Q is discharge (m^3/sec), $U1$ and $U2$ are the first two principal components of PCA for the stream or source, and the subscripts *s*, 1, 2, and 3 represent the stream and the three sources contributing to stream flow in the model.

Source contribution to stream flow during storm events in both dry (July 2009) and wet (December 2009) antecedent soil moisture conditions at UTC was determined using this approach. Antecedent moisture conditions were based on water table position in the riparian corridor prior to the storm event. According to U.S. Army Corps of Engineer and National Research Council criteria, wetlands are classified by the presence of a water table that is within 30 cm of the ground surface for at least 14 days during the growing season (USACE, 1987; NRC, 1995). For this study, dry antecedent moisture conditions were assumed when the water table fell below 50 cm of the ground surface and wet antecedent moisture conditions were assumed when the water table was within 50 cm of the ground surface.

RESULTS AND DISCUSSION

End-Member Mixing Analysis (EMMA)

Solutes considered for use in EMMA were limited to those believed to be behaving conservatively or somewhat conservatively in the wetland environment, based on the work of O'Brien and Eshleman (1996) and Donahue (1997).

Using Si, Ca^{2+}, Mg^{2+}, and Cl^-, 96% of the variability in the entire stream data set could be explained with the first three principal components. These transformations were used to create a three-dimensional *U*-space in which the *x*, *y*, and *z* coordinate were defined by the first three principal components. Stream and source data were inspected in this *U*-space to identify the potential end-members that contributed to stream flow.

Initially, this 3-D analysis required consideration of all potential end-members to contribute to stream flow. However, further analysis of the *U*-space showed that the deep groundwater source projected far from the stream matrix. This implied that there was very little interaction between deep groundwater sources and stream flow in UTC. Instead, a four source model consisting of precipitation, soil water, groundwater from the hyporheic zone, and groundwater from the upland meadow contained most of the stream data matrix, implying these were potential sources to stream flow in the watershed (Figure 2).

Several outliers occurred in the stream matrix that fell outside of the area bounded by the end-members. While using the median value for solute chemistry is adequate to represent the generalized end-member concentration, reliance on it to represent source concentration ignores any natural, temporal fluctuations in chemistry and has been argued to produce questionable estimates of source contribution on a small scale (Burns et al., 2001; Neal, 1997; Neal et al., 1997; McHale et al., 2002). However, EMMA, with source chemistry represented by median tracer concentrations, provides a means of discerning the relative contribution of sources to stream flow and is beneficial for hydrograph separation analysis (McHale et al., 2002).

Hydrograph Separation using EMMA

Variations of the four source model could be used to explain stream flow during varying antecedent moisture conditions. Hydrograph separation based on EMMA estimates was conducted for data from two storm events

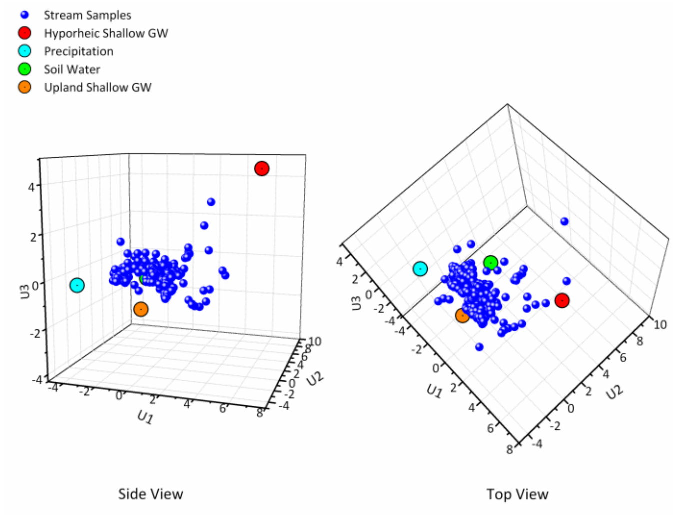

Figure 2. 3-D *U*-space projection of UTC stream data and four potential end-members.

that occurred in July 2009 and December 2009. The July storm was considered to occur during dry antecedent moisture conditions because depth to water in the riparian corridor was 71.6 cm below ground surface. Depth to water in the riparian corridor prior to the December 2009 storm event was only 25.9 cm below ground surface and thus, the storm was considered to have occurred during wet antecedent moisture conditions.

During dry antecedent moisture conditions, soil water, precipitation, and shallow hyporheic groundwater were identified as end-members to stream flow. The contribution from precipitation and soil water dominated stream flow during the storm event with precipitation's contribution comprising as much as 66% of the total stream discharge at the hydrograph peak (Figure 3). Conversely, soil water contribution was minimal prior to and during initial precipitation, but its maximum influence occurred during the falling limb of the hydrograph when it contributed as much as 65% of total stream discharge. The contribution from hyporheic shallow groundwater to stream flow was relatively stable during the storm event and was between 5-21% of total stream flow volume.

The influence of precipitation, as runoff, and soil water on stream flow during dry antecedent moisture conditions was consistent with previous research on lowland watershed hydrologic processes (Slattery et al., 2006). Because of the amount of precipitation preceding (as much as 24 mm in five days prior) and during the storm event, infiltration capacity may have been exceeded for the low-permeability soils surrounding Turkey Creek, leading to infiltration-excess runoff and shallow subsurface flow (Slattery et al., 2006). Soil water may be a significant source to stream flow as large volumes of water can be sequestered as soil storage if not lost to the atmosphere due to evapotranspiration (Sun et al. 2002). Following storm events, a rising water table can produce flow within the vadose zone, and discharge from soil water storage may result, possibly evident in the July 2009 storm event.

During wet antecedent moisture conditions, contributions from precipitation and upland and hyporheic groundwater could be used to explain stream flow. Hydraulically, these sources are also plausible as groundwater strongly influences stream flow during wet conditions, contributing to both surface (saturation-excess runoff) and subsurface flow (Harder et al., 2007).

Precipitation was the dominant source to stream flow during the storm, comprising as much as 70% of stream flow. Upland groundwater also acted as a significant source to stream flow; its largest contribution occurred at the peak flow over the hydrograph (Figure 3). These trends suggest that groundwater mounding and saturation-excess runoff were significant hydrologic processes influencing stream flow during wet antecedent moisture conditions at UTC (Slattery et al., 2006). The December storm event's occurrence during saturated soil conditions resulted in a rise in the water table position and shallow subsurface flow. As water moved from the upland site into the riparian corridor, the contributions from the shallow groundwater system and precipitation, as runoff and interflow, then dominated total stream flow as noted in the falling limb of the hydrograph.

The end-members identified through EMMA, as well as their contribution to stream flow during different storm events, were consistent with findings from previous research focused on lower coastal plain hydrology. Other conditions, such as evapotranspiration rates and rainfall intensity and duration could influence the source contribution during varying conditions and should be further examined.

Potential impacts of urbanization on stream flow

The model for stream flow developed at UTC, in which precipitation, soil water, and shallow groundwater are significant sources to stream flow, can be used to examine the future impacts of urbanization and land use change on lowland watersheds of the southeastern U.S.

The transition from forested or wetland dominated land cover to impervious surfaces may have significant impacts on source volume and contribution to stream flow. Research has demonstrated that the presence of impervious cover in a watershed minimizes infiltration processes and leads to a decrease in the amount of direct groundwater recharge to the local system (Leopold, 1968). Local groundwater sources and the amount of water available to water storage will be depleted and as a result, stream flow will be significantly impacted as the contribution from upland groundwater, hyporheic groundwater, and soil water sources are reduced.

These types of alterations to soil and groundwater sources will have implications on stream flow (Watts and Hawk, 2003; Poff et al., 2006). Sustained stream flow may be a rare occurrence, even during the dormant season. Instead, it can be expected that stream flow may only occur as a result of storm events. With infiltration processes inhibited by impervious coverage, any precipitation input into the watershed may be quickly discharged to the stream as storm water runoff (Wahl et al., 1997). Flashy conditions, in which heavy flooding can occur, will characterize stream flow even during low intensity storms. Without groundwater or soil water contributions to sustain it, stream flow may be short lived following the storm event and the stream quickly reverted back to no flow conditions.

Alterations to the local water budget described above have larger ecologic impacts. As sensitive, wetland ecosystems are modified by fluctuations in groundwater and surface water availability, indirect impacts, such as increased nutrient, sediment, and pollutant loading as a result of flashy stream flow will also impact ecosystem vitality (Farahmand et al., 2007). These stressors may lead to the modification or loss of plant and animal biodiversity and have larger ramifications on the local and regional food web, much of which has been described elsewhere (Schueler, 1994; Holland et al., 2003; and others).

Alterations to lowland watershed's sources and stream flow will also impact coastal communities. Already, there is a high demand placed on water resources to meet a variety of municipal, economic, and industrial needs (USGS, 2010). This type of demand placed on a depleted ground and surface water source leads to a variety of water management issues that may be further exasperated by burgeoning population and climate change (Carbone and Dow, 2005). Given these potential impacts, it is imperative to determine a series of best management practices that can minimize the influence of urbanization on lowland water groundwater and surface sources.

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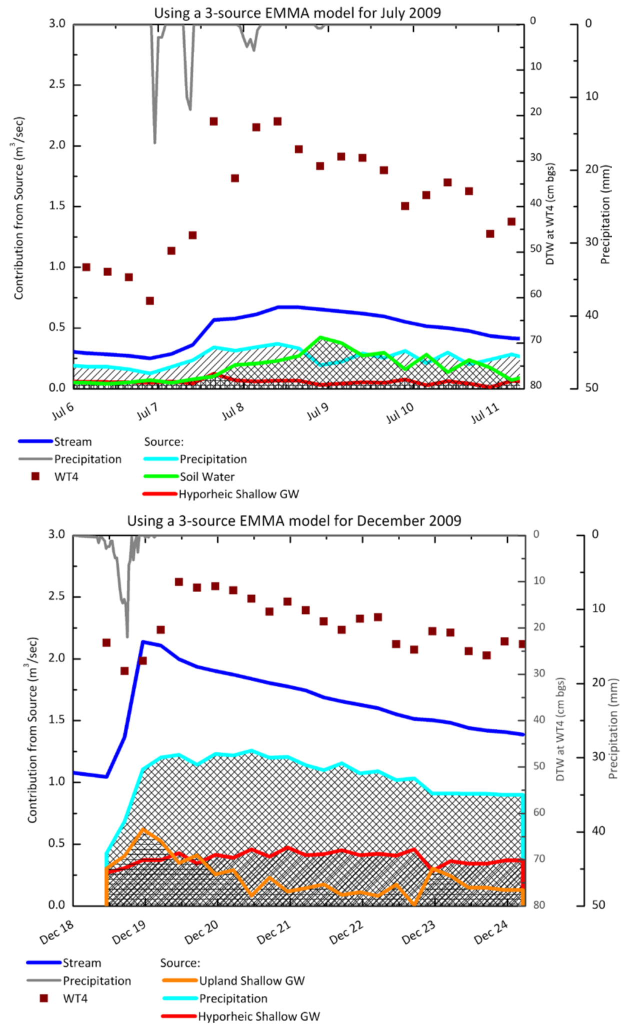

Figure 3. Hydrograph separation of stream flow during July (top) and December (bottom) 2009 storms using EMMA derived estimates for source contribution in UTC. Groundwater levels in the riparian corridor are also included to monitor moisture conditions during the hydrograph period.

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