THE EFFECTS OF STORMS ON STREAM WATER QUALITY IN A KARST LANDSCAPE

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Abstract. A need exists to develop predictable relationships between hydrologic characteristics and water quality for Coastal Plains streams and the fundamental hydrographic/water chemistry responses to storms in karst regions. Nine storms and resultant runoff were sampled in Ichawaynochaway Creek in southwest Georgia to quantify these relationships. Stream hydrologic response varied with seasonal antecedent conditions, precipitation amount, and duration. Both the intensity of a storm and the quantity of water generated resulted in variable non-point source runoff and/or dilution of baseflow conditions. Increases in dissolved concentrations were typically seen for ammonium, orthophosphate, sulfate, potassium, and dissolved organic carbon. Alterations were generally consistent with floodplain inundation rather than erosive surface runoff from agricultural land. Changes in chemistry were affected by the base flow water quantity and quality, timing of source waters, and biological activity. Decreases in concentration were typically seen for alkalinity, pH, conductivity, nitrate, calcium, magnesium, and sodium

INTRODUCTION

Watershed planning and management is evolving in Georgia. To wisely use and sustain our rivers in Georgia, will require knowledge of the hydrologic and biogeochemical processes and watershed characteristics responsible for stream flow and water quality. Biogeochemical processes include release (weathering, fertilization), transformation and loss (denitrification, biotic uptake), and transport (flow paths). Evaluating the role of natural features (soils, geology, landcover, source waters, and flow paths) and human factors (water use, landuse, structures such as dams) in large watersheds will be challenging.

Evaluation of storm runoff hydrology and biogeochemistry provide insights to watershed processes and landuse effects. Source waters and transport paths can be identified using hydrograph separation techniques (Mulholland 1993). Biogeochemical input from variable source areas (wetlands, riparian zones, forests, agricultural fields) often are chemically distinct (Arheimer and Liden 2000). Organic or reduced forms of nutrients are associated with wetlands while particulate and oxidized forms are associated with agricultural lands. Because most source waters have distinct chemical composition and ionic concentrations, chemistry changes over a storm can be used to identify the relative influence of overland flow, shallow groundwater or soil water, and deeper groundwater aquifers (Johnson et. al. 1969, Mulholland 1993). Seasonal variation in hydrogeochemical response can occur and is related to hydrologic antecedent conditions and biotic processes (Peters 1994).

In Coastal Plains watersheds, low topographic relief results in extensive riparian wetlands, high surficial groundwater tables, and predominance of shallow groundwater lateral transport over surface transport. Stream hydrologic response is greatly influenced by this surficial groundwater head. Riparian wetland drainage often results in low ionic content, high dissolved organic matter, low pH and poorly buffered streams. However when significant limestone deposits are located near the ground surface, the degree of aquifer contribution and dissolution of the limestone bedrock will affect stream quality. Limestone aquifer water has higher ionic content, basic pH, is highly buffered, and nutrients that are inorganic and oxidized. An understanding of storm event responses of Coastal Plain streams in Georgia has not been developed. Results are summarized for nine selected runoff events that occurred in the Ichawaynochaway Creek Watershed from October 1994 through March 1998.

STUDY SITE

Ichawaynochaway Creek watershed is located primarily in the Dougherty Plain district of the Gulf coastal plain in southwest Georgia. This region is covered by an undifferentiated surface layer of sands and clays from 1 to 40 meters deep (Hayes et. al., 1983). The soils are generally loamy sands exhibiting moderate permeability. Underneath this layer lies the Ocala limestone, an extensively fractured and porous rock layer with high hydraulic transmissivity. This Ocala limestone is the principal water bearing strata for the Floridan Aquifer. The Floridan aquifer is seasonally recharged in the Dougherty Plain by rainfall percolating through the undifferentiated overburden. The Floridan aquifer discharges into streams that incise the Ocala limestone (Hicks et al 1987). Thus, baseflow in Ichawaynochaway Creek and its tributaries is maintained by discharge from the Floridan aquifer.

After originating in an extensive swamp and wetland system, Ichawaynochaway Creek travels approximately 100 km south before discharging into the Flint River. In 1995, the watershed was 46% agriculture, 35% forest and 19% wetlands. An intact riparian zone occurs along most of the creek and its tributaries. Broad floodplains occur in the headwaters through the middle reaches. The floodplains narrow as creeks incise into the limestone. A major swamp complex occupies 78,000 in the mid to lower reaches of Chickasawatchee Creek, a tributary of Ichawaynochaway Creek. This wetland complex is a major recharge and discharge area for the Floridan aquifer

Average daily discharge for Ichawaynochaway Creek at Milford (69 km downstream from the headwaters) is 22 m^3/sec. Average monthly discharges range from a low of 14.1 m^3/sec in September to a peak 36.5 m^3/sec in February (USGS Water Resources Data 1939-1999). Chickasawatchee Creek (located 9 km upstream from the confluence with Ichawaynochaway Creek) average daily flow is 9 m^3/sec (1995-1999). Average daily flow for the Ichawaynochaway Creek at Elmodel (located 16 km south of Milford) is 35 m^3/sec (1995-1999). For the 5 year study period, stream flow in Ichawaynochaway Creek at Elmodel was 64% from upstream in Ichawaynochaway Creek, 26% from Chickasawatchee Creek, and 10% from ground water inflow. Average daily discharge at the sampling site (located 10 km south of Ichawaynochaway Creek at Elmodel) was 38 m^3/sec (1995-1999).

METHODS

Nine storms were sampled. Hourly measurements of dissolved oxygen, temperature, conductivity and depth were obtained using Hydrolab Datasonde 3 and 4 Multiprobe Loggers. Water samples were collected every four hours using ISCO 3700FR refrigerated samplers. Alkalinity and pH were determined using a Mettler DL12 titrator. Samples for chemical analysis were filtered through 45 um Whatman GFS glass microfibre filters. Therefore, nutrients and cations presented in this paper represent the dissolved fraction. Nutrient concentrations (nitrate, ammonium, phosphate, sulfate, and chloride) were determined using flow-injection colorimetric methods on Quik-Chem 8000 and AE Automated Ion analyzers (Lachat Instruments). Dissolved carbon (total, inorganic, and organic fractions) was determined with a Shimadzu TOC-5050 analyzer. Cation analyses (calcium, magnesium, sodium, potassium, iron and aluminum) were conducted on a Perkin-Elmer 5100 PC Atomic Absorption Spectrophotometer equipped with a Zeeman graphite furnace. Microsoft Excel was employed for graphical and regression analyses.

RESULTS AND DISCUSSION

Hydrologic response to a given rainfall input varied with baseflow condition. Storms were sampled which represented three hydrologic conditions: summer baseflow, groundwater recharge in the fall and winter baseflow. Lowest stream antecedent conditions (i.e. lowest pre-storm stream flow) occurred during seasonally low baseflow (Table 1). Change in flow per inch of rainfall was lowest during summer baseflow. Runoff per inch was 1.5 times greater during rising groundwater tables and 3.9 times greater during seasonal high baseflow than summer baseflow conditions.

Stream temperature changes during storms indicated several source waters contribute to the storm hydrograph. Seasonal differences occurred in the number and timing of those waters. Two water sources were indicated by temperature changes during February 1996. Temperatures increased with increasing storm runoff and reached a maximum 20 hours after peak discharge. Water temperature remained constant during the storm and baseflow recessions. During a summer (June 1996) storm, three water sources were indicated. Temperature initially declined during the first half of the ascending limb, then increased until 20 hours after peak discharge, remained constant during storm flow recession, and then declined during baseflow recession.

In karst terrains, base flow is maintained by a significant inflow of aquifer water. In this region, groundwater has high pH, alkalinity, calcium, magnesium, sodium, and nitrate (Entrekin 1997). Waters contributing to pre-storm baseflow pH,

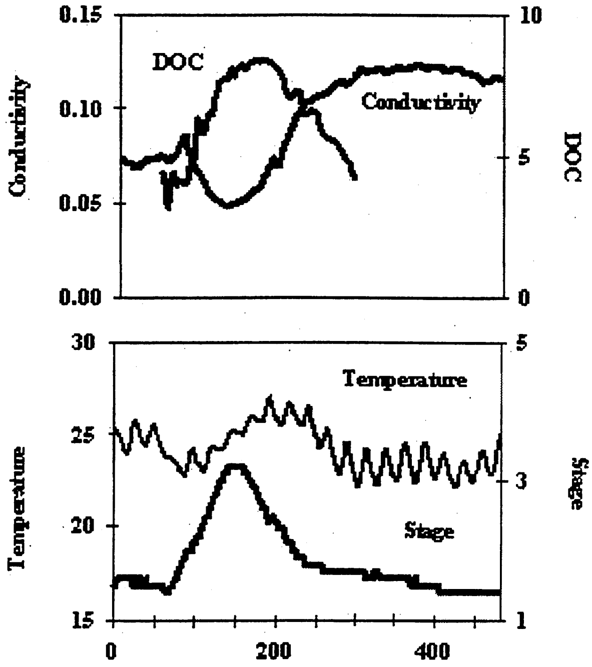

Figure 1. Ichawaynochaway Creek at Newton changes in stage (meters), temperature (celcius), dissolved organic carbon (DOC – mg/l), and specific conductivity (millisemins/cm) for a storm occurring in June 1995.

alkalinity, calcium, magnesium, sodium, chloride, and nitrate in Ichawaynochaway Creek at Newton were a mix of aquifer water, surficial ground water, and waters from the upper basin. Baseflow concentrations of calcium, magnesium, sodium, alkalinity, pH, chloride, and nitrate were higher than rainfall concentrations yet lower than ground water (rainfall concentrations found in Entrekin 1997). As an example, average pre-storm baseflow calcium concentration was.45% of aquifer concentrations but 75 times greater than average rainfall concentrations. Average pre-storm stream water nitrate was 20% of the ground water concentration yet 35 times the average rainfall concentrations.

For several storms, contributions to flow from the wetted perimeter of the stream are indicated during the first few hours (Figure 1). Conductivity, pH, alkalinity, and calcium increased rapidly over baseflow then declined as stream flow increased. They are significantly higher in surficial ground water adjacent to the stream than stream or aquifer water (Entrekin 1997). These changes in chemistry coincided with the change in water temperature previously discussed.

Dilution of ions originating from ground water occurred consistently for all storms. After the initial flush of ions, calcium, magnesium, sodium, alkalinity, pH, chloride, and nitrate varied inversely with storm runoff. Minimum concentrations often coincided with maximum peak discharge. The rate of ion decline was generally proportional to the rate of flow increase. The June 1995 storm was representative with significant ion-flow regression coefficients ranging from 0.80 (Na) to 0.95 (K, NO_3) on the rising limb and 0.90 (K) to 0.97 (Ca, Na) on the recession limb of the hydrograph. Calcium, magnesium, sodium and nitrate declines were slightly greater than flow increases.

Although these ions were diluted, runoff became enriched as waters moved across the landscape. The minimum storm concentrations were much greater than rainfall concentrations. Solution of soil minerals; exchange of hydrogen for calcium, magnesium, sodium; leaching of organic matter; and dissolution of limestone are potential sources.

During storm recession, ground water sources and drainage from Chickasawatchee Creek are important. Alkalinity, pH, conductivity, and calcium increase with increasing contributions from groundwater. Contributions from Chickasawatchee Creek are important during the early phases of flow recession. Chickasawatchee Creek water is higher in these constituents than water draining from Ichawaynochaway Creek at Milford (Entrekin 1997). Chickasawatchee Creek discharge occurs near or past peak discharge in Ichawaynochaway Creek at Newton.

Additional dissolution of limestone may occur during storms. As the stream approaches baseflow; alkalinity, pH, conductivity, and calcium increase to levels greater than base flow concentrations prior to the storm. Acidic rainfall and soil acids leaching with percolation may dissolve the Ocala limestone as water moves to the creek. For storms, in which, baseflow is higher after the storm than before, this increase may be due the greater proportion of ground water supporting stream flow. However, these increases occur after storms in which the stream returned to base flows similar to those prior to the storm.

Processes within the watershed are important in maintaining base flow concentrations of ammonium, sulfate, phosphate, potassium, and total organic carbon. Baseflow concentrations in stream water are higher than concentrations in either ground water or rainfall. Aquifer water discharging through seeps, wetland drains, or swamp complexes like the Chickasawatchee has ample opportunity to mobilize and transport these water quality constituents. Total organic carbon is

Table 1. Storm characteristics for each storm sampled

Dates	Rain (inches)	Base flow (cfs)	Peak storm flow (cfs)	Baseflow Stage Change (m)	Time to Peak (hr)	Runoff Duration (hr)	Nitrate Mean (mg/l)	Nitrate Maximum (mg/l)	Nitrate Minimum (mg/l)	DOC time to peak (hours)	DOC lag (hours)
Oct-94	4.8	598	4320	2.1	50	151	192	391	111		
Feb-95	4.0	788	8730	4.9	96	196	328	449	194	148	52
Jun-95	4.3	362	2790	1.6	60	245	443	810	168	112	52
Nov-95	0.7	607	805	0.3	83	378	276	367	222	127	44
Feb-96	2.2	732	1940	0.9	74	122	344	516	222	130	56
Feb-97	3.1	805	3040	1.6	83	205	334	588	209	124	41
Oct-97	2.8	117	499	0.6	117	233	734	995	365	143	26
Mar-98	6.0	1260	18,800	8.0	91	310	302	441	37	106	15

greater in waters draining Chickasawatchee Swamp than other tributary streams in the watershed (Golladay and Battle, this conference). Both total organic carbon and ammonium are higher during wet or flooded watershed conditions.

Ammonium, sulfate, phosphate, potassium, and total organic carbon concentrations increase in a predictable manner with flow. All generally increase over the storms with peak concentrations around the peak in discharge. Dissolved phosphate maximum concentration occurred prior to the peak. Sulfate and total organic carbon generally reached maximum concentrations approximately two days after peak discharge in Ichawaynochaway Creek at Newton (Table 1). Total organic carbon and sulfate concentrations were highest when drainage from the Chickasawatchee Creek was greatest. Ammonium maximum concentrations varied around peak discharge. Ammonium concentrations generally varied similar to phosphate. During several storms, a secondary ammonium peak occurred during storm flow recession. Baseflow concentrations of these ions were higher after the storm than baseflow concentrations prior to the storm.

Mobilization of these constituents from the watershed soils and wetlands is substantial given they all increase with discharge. Drainage of large swamp systems like the Chickasawatchee Creek Swamp, riparian wetlands, and decomposing organic material of the soil matrix are all potential sources of ammonium, sulfate, phosphate, potassium, and total organic carbon. Wetland drainage is clearly important for transport of ammonium, sulfate, potassium, and total organic carbon with concentrations greatest during storm flow recession and coinciding with peak drainage from the Chickasawatchee Swamp. Mobilization of ammonium and phosphate from the soil matrix and transport via surface and subsurface runoff is indicated from the peak ammonium and phosphate concentrations prior to peak discharge.

SUMMARY

Water quality changes associated with storm runoff can be used to identify potential water sources contributing to flow in karst watersheds. Baseflow concentrations, temperature and conductivity indicate flow is support by a combination of subsurface soil drainage, surficial and aquifer ground water, and wetland drainage. During low flow periods, initial drainage from the wetted stream perimeter is important during the first few hours of storm discharge. A rapid spike in dissolution products of limestone occurs during this period. During high flow periods, no chemical change was observed in the first few hours of the storm runoff. The wetted perimeter still may be contributing to flow but the ionic content may be too low from seasonal inundation or repeated storm drainage to detect a change. As the watershed becomes wetted with rainfall and storm runoff increases, contributions are largely from surface or subsurface non-point source runoff. Ground water derived constituents are diluted and subsurface soil constituents are enriched. Given the sandy soils and low topography of this region, subsurface runoff is likely a greater source than surface runoff. As the watershed drains and storm flow recedes, wetland drainage is important. Constituents associated with wetland runoff are dominant during this period. In the later stages, stream discharge is supported by decreasing quantities of wetland drainage and increasing proportions of ground water inflow. Limestone dissolution products, pH and conductivity increase to above prestorm conditions during this period.

Significant mobilization of nutrients, cations, and dissolved organic carbon occurs during storms. Concentrations were always greater than would be predicted by changes in water volume. These constituents have multiple sources in the watershed. They originate from the wetted perimeter of the stream, soils, limestone bedrock, and decomposing organic material.

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