

# APPLICATION OF GEOCHEMICAL END-MEMBER MIXING ANALYSIS TO DELINEATE WATER SOURCES IN A LOWLAND WATERSHED

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**Abstract.** Water fluxes in lowland watersheds are influenced by streams, groundwater, soil type, topography, precipitation, evapotranspiration, etc. However, the relative influence of each of these factors is usually hard to ascertain based on hydrology alone. The overall goal of our research is to understand watershed dynamics in lowland watersheds in response to storm events as a function of soil type, depth to water table, and topography. We used an end-member mixing technique involving geochemical data to delineate the influence of various sources of water in the Turkey Creek Watershed, which is in the Francis Marion National Forest near Charleston, SC. The soils in this watershed range from moderately well-drained to poorly-drained and are influenced by seasonally high water tables. This watershed is also characterized by very flat slopes and overall elevation of 4-14 m above sea level. We installed a series of water table wells and piezometers in the stream bed, at the margin areas adjacent to the riparian zone, and in the upland areas away from the riparian zone. Water samples from the wells, the streams, and rainfall were collected on a regular basis and were analyzed for major cations and anions. Preliminary rainfall data indicate that major ion concentrations were substantially lower than those measured in the well and stream water samples. Additionally, some well water contained higher levels of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  compared with other wells possibly due to influence of a deeper groundwater system of higher salinity. We hypothesize that storm events produce flushing of shallow groundwater to the streams, but the deeper groundwater system may not be connected to the stream. Using these data we are developing a geochemically constrained water budget model that could be applicable for such lowland watersheds to complement pure hydrological models.

## BACKGROUND

The influence of precipitation, groundwater, soil water, soil type, topography, evapotranspiration etc. on low gradient coastal watersheds has implications in diverse fields such as carbon capture dynamics, watershed man-

agement, and urban planning. However, it is not clearly understood how specific water sources such as precipitation, stream water, and groundwater influence watersheds in such environments. An approach based on delineating water sources using water budget analysis does not provide definitive answers. Combining water chemical data to hydrological data is requisite to establishing a comprehensive watershed hydrological model.

End member mixing analysis (EMMA), which exclusively uses water chemical composition to identify contributions of components in a hydrological budget, has been used to identify specific contributions to stormflow (Mulholland 1993; Tardy et al. 2004). Briefly, this technique involves a simple mixing model for identifying water reservoirs (end members) that contribute to a stream or a wetland and have chemical compositions that are different, relatively constant, and that constrain the observed variation in stream chemistry (Mulholland 1993). For example, if three specific end members are identified as contributing to a stream, and if each of these end members have specific cation and anion concentrations, the fraction of the stream discharge that is contributed by each end member can be calculated with the help of the following three simultaneous equations:

$$f_1 + f_2 + f_3 = 1 \quad (1)$$

$$f_1[A]_1 + f_2[A]_2 + f_3[A]_3 = [A]_S \quad (2)$$

$$f_1[C]_1 + f_2[C]_2 + f_3[C]_3 = [C]_S \quad (3)$$

Where,  $[A]$  and  $[C]$  are concentrations of anions and cations, respectively, and the subscripts, 1, 2, and 3 refer to the three end-member components, the subscript  $S$  refers to the stream water (mixture), and  $f$  refers to the fraction of each component contributing to stream water. These equations are solved for every time at which there was stream water chemistry data over the storm hydrograph.

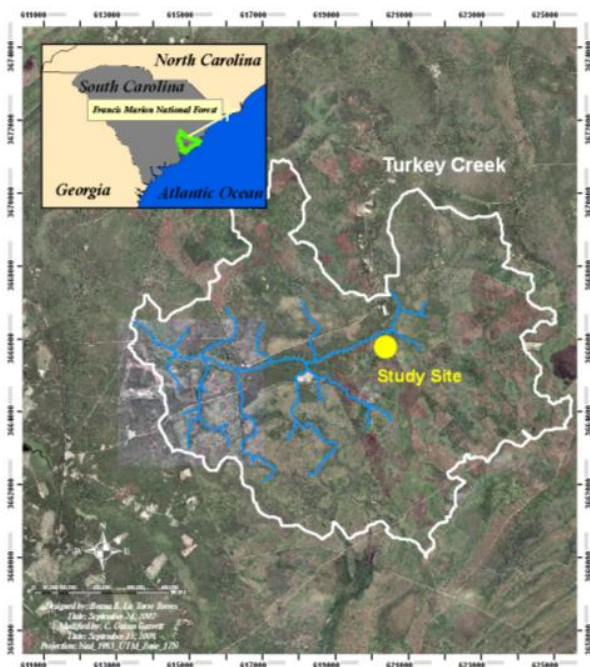
Specific objectives of this study are to (i) develop geochemical analytical methods to delineate contributions of shallow interflow or soil water, precipitation, and deep groundwater to the wetland and (ii) expand this study to

larger watersheds and onto other wetland environmental settings to build a more comprehensive model of the role of hydrology and geochemistry on wetland carbon flux. We hypothesize that the analysis of multiple combinations of anions and cations can help identify specific reservoirs that contribute to watersheds. Further, we hypothesize that combining this technique with hydrological data will help develop a comprehensive watershed model.

## MATERIALS AND METHODS

### Site Description

The proposed EMMA technique is being applied to a coastal watershed, specifically, a forested riparian wetland within the 7000-hectare Turkey Creek watershed (Fig. 1) located in the Francis Marion National Forest, Berkeley County, (33.15° N, 79.8° W), northeast of Charleston, South Carolina (SC). The predominant land use (> 90%) in the watershed is forest, consisting of mixed conifer-deciduous tree stands in the uplands and predominately deciduous tree stands in the wetlands. The other 10 % of land use includes agriculture, open fields, and roads. Soil types range from moderately-well drained fine-loamy, siliceous, subactive, thermic Aquic Paleudults of the Goldsboro series to poorly-drained fine, mixed, active, thermic Typic Albaqualfs of the Meggett series. Soil series information was collected from SSURGO database of the National Resources Conservation Service (NRCS, 2003) and by direct verification in the field.



**Figure 1: Location of Turkey Creek watershed (white boundary), the Turkey Creek (blue lines), and the study site in the Francis Marion National Forest, SC.**

### Methods

We installed four water table wells (about 3-11 ft depth) and four drive-point piezometers (10-20 ft depth) to supplement an existing water table well and a piezometer nest near a weather station at this site. After the wells and piezometers were developed, water samples were obtained for chemical analysis over the course of two summers in 2007 and 2008. Water level measurements in most of the wells and piezometers were recorded continuously at either a one-hour interval for water-table wells and shallow piezometers or at a four-hour interval for the deeper (> 20 ft below ground) piezometers using Solinst® Leveloggers (Solinst, Canada). Standard sampling protocols were followed to purge well and piezometer tubing of approximately three volumes to clear stagnant water and obtain pore water for chemical analysis. In some cases during dry periods and in areas of low-permeability materials, the available water in water-table wells was less than three volumes and such samples were recorded for future scrutiny of the data.

The collected water samples were centrifuged at 5000×g to remove suspended sediments and analyzed for cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) and anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ ) using an ion chromatograph (Metrohm, USA) as per standard US Environmental Protection Agency and American Water Works Association standard water test methods (Eaton et al. 2005; EPA 1993).

## RESULTS AND DISCUSSION

Water table level and precipitation data from summer 2007 and 2008 indicate that there is very good correlation between precipitation and groundwater levels in the water table wells and the shallow piezometers. The water table levels in these wells responded very quickly following a precipitation event – however, the response was muted in some wells compared with other indicating differences in the soil types into which the wells were installed. There was little correlation between the precipitation and the deeper piezometers. There was a drastic but consistent drop in water table levels over the course of both summers due to extended drought periods as well as increased evapotranspiration (Fig. 2). Water table levels recovered very quickly following storm events, but not to the pre-summer levels. On average, storm events producing greater than 10 mm rainfall caused a rapid change in water table levels with little lag time.

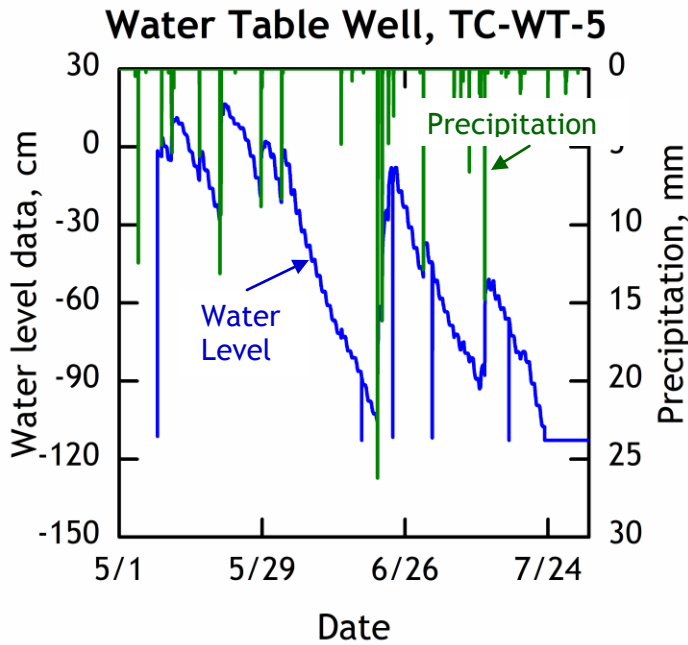


Figure 2: Water level response in water table well TC-WT-5 to precipitation between May 2008 and July 2008.

Extended drought during the two summers sampled also limited the volume of water available for chemical analysis. Water was only present intermittently in the Turkey Creek, while some of the water table wells and some piezometers did not yield any samples over extended periods of time. However, following storm events nearly all water table wells and most piezometers yielded sufficient water for subsequent chemical analysis.

Ion analysis of water samples revealed that all ions were present in all samples analyzed. However,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  were the dominant ions in most water samples. In general, lower concentrations of all ions were measured in water table wells (Fig. 3) compared with those in piezometers (Fig. 4). In most cases, the ion concentrations were relatively consistent throughout the baseflow period. Small spikes in concentrations were observed following storm events. For simplicity, all measured cation and anion concentrations were converted to meq/L and expressed as total cation or anion concentrations in this paper. An advantage of expressing data in this form is that the charge balance can be compared graphically.

The charge balance indicates that sum of all positive (cations) and all negative (anions) charges are equal in any natural water system. In cases where this balance is not maintained, other ions that were not included in the balance have to be considered. The ion chemistry data from the water table data indicates that charge balance may exist for several wells (Fig. 3).

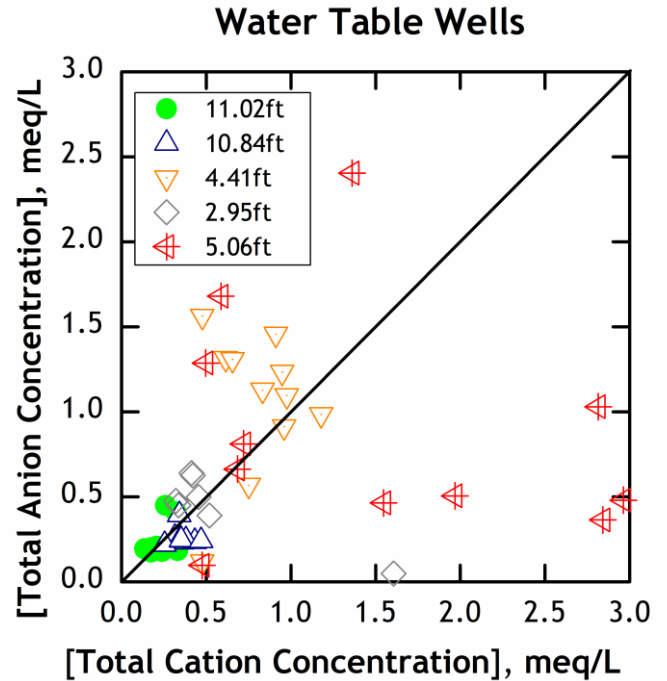


Figure 3: Major ion chemistry in water samples from water table wells in the study site. Anions measured include  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  and cations measured include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . Slope of 1:1 for comparing concentrations of anions and cations. Legends indicate depths of the water table wells.

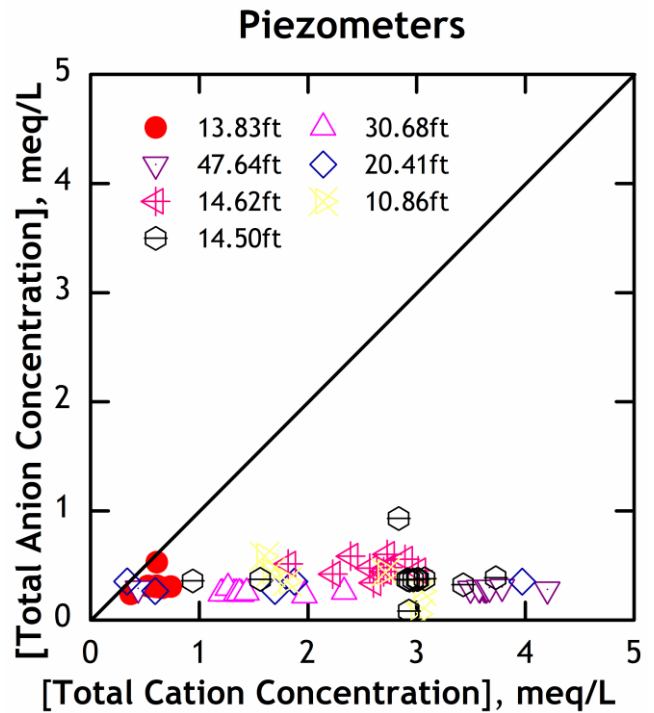


Figure 4: Major ion chemistry in water from piezometers at study site. Anions include  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ ; cations include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . Slope of 1:1 for comparing concentrations of anions and cations. Legends indicate depths of the piezometers.

In some cases the concentration of cations was greater than the concentrations of anions, indicating that perhaps other anions are to be considered. In case of the piezometers, the charge balance is non-existent (Fig. 4). The concentrations of the cations were significantly greater than those of the anions indicating that other anions that were not measured were present in significant quantities in these samples. While these piezometers do not penetrate the carbonate aquifer underlying Turkey Creek watershed, there is perhaps a strong influence of water from this deeper aquifer. This influence can potentially contribute significant amounts of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  to water at shallower depths. Whether this influence extends all the way to the surface streams is yet to be determined.

### FUTURE WORK

The hypothesis that the deeper aquifer is contributing to the surface streams will be tested by analyzing the water samples for  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . Furthermore, soil water will be collected at this site using suction lysimeters and those samples will be added to the EMMA model for this site. Monitoring of the existing water table wells and piezometers will continue through the following months to gain a more complete picture of the system as a function of seasonal changes. Once all data is available the end members will be clearly delineated and the influence of each end member on the streamflow will be calculated from the method outline in Equations 1-3.

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