Using Water Chemistry Data to Assess Stormwater Pathways in Lowland Watersheds

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ABSTRACT. Forested lowland watersheds of the lower coastal plain (LCP) are being developed for residential, commercial, and industrial use at an increasing rate. We explored the use of end-member mixing analysis (EMMA), a hydrochemical technique, to better understand water flow processes in the LCP. We compared results from chemical hydrograph separation (CHS) from EMMA and a physical hydrograph separation (PHS) approach based on falling hydrograph limb regression.

These approaches were applied at Watershed 80 (WS-80), in the Santee Experimental Forest near Cordesville, SC, which drains 200 hectares. Samples from water-table wells, piezometers, lysimeters, rain gauges, and streamwater samplers were assessed for major cation and anion concentrations, which serve as natural chemical tracers.

Both methods provide estimates of storm-event flow: quickflow by PHS and rainwater contribution by CHS. Results indicate a high level of consistency between the approaches for some storms. However, other storms show markedly differing results. These results illustrate the complexity of runoff production dynamics in LCP watersheds and suggest that using parallel methods provides a more nuanced understanding of hydrological processes.

Our findings suggest that a rough understanding of groundwater flow processes can be accomplished for low-order lowland watersheds in periods of less than one year using a rapid deployment of EMMA. Due to the shallow water table, piezometers can be installed by hand-auguring. Lysimeters and rain gauges are inexpensive and easily installed. Streamwater samples can be collected manually, or preferably with a sampler. Sample processing can be contracted to an academic or private laboratory, and data processing can be performed with free software. These findings show that a hydrogeochemical approach to understanding lowlands watersheds is not cost- or time-prohibitive, and can provide critical information to land managers and policymakers who oversee the urbanization of these watersheds.

INTRODUCTION

The Lower Coastal Plain (LCP) of the United States is undergoing dramatic and rapid change. Development is converting forested, minimally developed, and rural landscapes into urban, suburban, and exurban areas. Key changes that result from such development include: removal of vegetation, covering of bare earth with surfaces of limited permeability, and modification of stream channels; all potentially result in increased stormwater runoff. From 1973 to 1994, urbanized land use in the Berkeley/Charleston/Dorchester tri-county region grew by 256%, even though population during this time only grew by 41% (BCDCOG, 1997). Allen and Lu (2003) predicted that between 2000 and 2030, urbanized land use in the tri-county region will triple. Unless significant mitigation efforts are made, between 2000 and 2025, an additional 866 miles of streams statewide are likely to be in areas where they will suffer severe degradation, that is, where impervious land cover is greater than 10% (Exum *et al.*, 2005). As land is developed, forested lands are lost. This is a particular concern in the southeastern USA, since forecasts indicate that 90 percent of forested land use loss in the United States from 1997 to 2060 will occur in the East, and more than half in the South (Wear, 2011).

To better understand the effect of change on these watersheds, it is critical to understand how these watersheds function in their natural state. However, the hydrologic processes of forested coastal lowland watersheds in the southeastern U.S. are not fully understood (Kirchner, 2003; Winter *et al.*, 2003; Amatya *et al.*, 2006). Geologic, topographic, climatic, and meteorological factors combine to make estimations of runoff in response to storm events difficult.

Physical hydrological approaches for studying hydrological processes and water-resource issues have long been employed. In this study, we explore the use of a hydrochemical technique to give a fuller understanding of groundwater/surface-water interactions and stormwater pathways in a minimally developed, first-order watershed. We hypothesize that using physical and chemical approaches in tandem will give the clearest understanding of these subtle processes. This information is critical for developers and water-resource managers in an era of rapid urbanization.

PROJECT OBJECTIVES

In this paper we will demonstrate the use of natural water chemistry to elucidate hydrological processes of coastal-plain watersheds through the use of chemical hydrograph separation; compare results from chemical hydrograph separation to a physical hydrograph separation technique, and thereby describe benefits of both approaches; and describe an approach for a rapid deployment to study water chemistry at a small watershed.

METHODS

Site Description

The Santee Experimental Forest (SEF) is a minimally developed and lightly managed forest within the Francis Marion National Forest near Charleston, SC, and has been used for science and management research since 1937 (Amatya *et al.*, 2003). The control watershed of the SEF, WS-80 is a first-order watershed with a small, ephemeral, channelized stream. The soils are primarily clays and loams. Historically used for rice cultivation, WS-80 is now composed of a forest canopy of pine-hardwood (39%), hardwood-pine (28%) and mixed hardwoods (33%) (Amatya and Radecki-Pawlik, 2007).

The site is instrumented for thorough hydrological and hydrochemical analysis. Shallow water-table wells were used to track the depth of the water table throughout the year. Piezometers of varying depths allow for pressure (aquifer head) assessment and sample collection at specific depths below the ground surface. Soilwater suction lysimeters (Soilmoisture Equipment Corp., Santa Barbara, CA) collected water from the vadose zone by vacuum pressure. Streamwater auto-fraction collectors from Isco (Teledyne Isco, Inc., Lincoln, NE) collected periodic stream samples. Automatic data logger modules (Solinst Canada Ltd, Georgetown, ON) recorded water table position hourly.

A weather station (Campbell Scientific, Inc., Logan, UT with CR10X data loggers) was operated by the US Forest Service Center for Forested Wetland Research in Cordesville, SC, and included an automatic tipping bucket rain gauge to track rainfall quantity and storm intensity. Manual rain gauges (Forestry Suppliers Inc., Jackson, MS) measured and captured rainfall and forest-canopy throughfall.

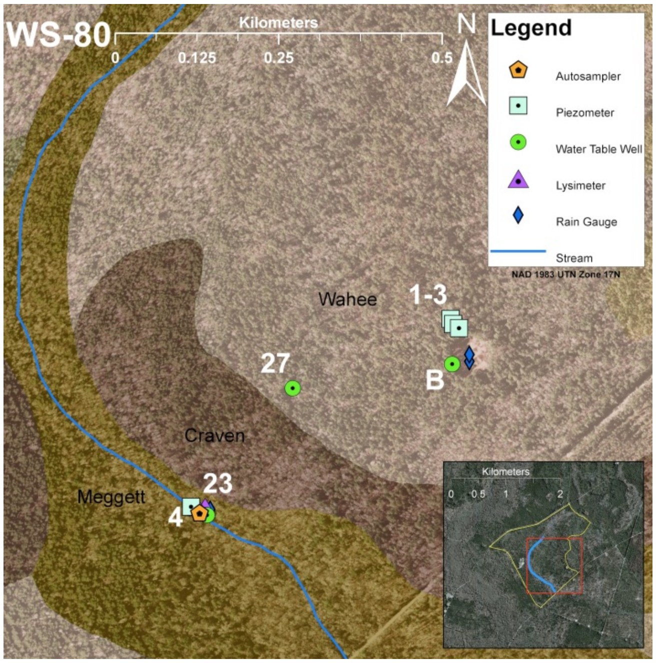

Figure 1. Watershed 80 (WS-80) at the Santee Experimental Forest, 30 miles northeast of Charleston, SC. This watershed is instrumented with water-table wells, piezometers, suction lysimeters, rain gauges, a auto-fraction stream-water sampler, and a weather station. This infrastructure is identified by site numbers, shown in the image above as white numbers, from high to low elevation: 1-3, B, 27, 23, and 4. Site 1 is at N33.1491, W79.7889.

Stream flow was calculated from stage height at a compound outlet weir less than 1 km downstream from the stream sampling location, at the watershed outlet. The stream ponds upstream of the weir, causing a muted hydrograph effect, as flow slows when it joins this ponded area. Flow rate is calculated using an established stage-discharge at this weir by the US Forest Service and was a good estimate of stream flow from the watershed (Harder *et al.*, 2007).

Sampling and data collection occurred on a roughly monthly basis from 2009 through 2011 and quarterly during 2011. Sampling before and after storm events was a priority.

Physical Hydrograph Separation (PHS)

Using a process developed for the coastal plain (Williams, 2007), quickflow and baseflow quantities were estimated based on regression analysis. This approach assumed storm flow and sustained baseflow to be two linear reservoirs discharging at different rates. Baseflow was modeled according to Maillet's (1905) single linear reservoir discharge model: $Q(t) = Q_0 * e^{(-t/k)}$. Linear regression of log(Q) estimated baseflow for a given storm event. Flow in excess of baseflow was assigned as storm flow, or quickflow.

In the absence of quickflow, the logarithm of stream flow decreased linearly. If the logarithm of flow was decreasing non-linearly, there was quickflow contributing to the stream. This method gave estimates of quickflow with only stream flow data. For full treatment of this method, see Rogers (2010) and Epps *et al.* (2012).

Chemical Hydrograph Separation (CHS)

Water samples were filtered with 0.45 µm Millipore-HP MPES syringe filters, and prepped by standard methods for analysis on an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500cx, Agilent Technologies, Santa Clara, CA) for determination of total concentrations of Ca, Na, K, Al, Mg, Si, Fe, and Mn. ICP-MS detection limits were less than 0.10 ppm. Samples were also run on an ion chromatograph (IC, Metrohm, Riverview, FL) for anion concentration determination, including F^-, Cl^-, Br, NO_3^-, PO_4^{3-}, and SO_4^{2-} using standard methods (Eaton and Franson, 2005). IC detection limits were less than 0.50 ppm.

To elucidate data trends, principal components analysis (PCA) was performed using open-source software *R* (The R Foundation for Statistical Computing, http://www.r-project.org). PCA was performed on the stream samples, to study how natural tracers change over time, and medians of potential water sources (or *end-members*) were transformed based on the PCA results. The PCA results allow for choosing end-members that contribute to stream flow, such as upland groundwater, riparian groundwater, streambed groundwater, soilwater, and rainwater.

Using the PCA results, end-member mixing analysis (EMMA) was performed (Christophersen and Hooper, 1992; Burns *et al.*, 2001; Garrett *et al.*, 2012). A series of linear equations were solved for each stream sample, using Mathematica 8 (Wolfram Research). Solving these equations for each stream water sample, the fraction of total flow from each end-member was calculated throughout storm events. With the resultant data, hydrographs were constructed with the end-member contributions separated, to show the relative influence of each end-member during the study period.

RESULTS AND DISCUSSION

Comparing Physical and Chemical Hydrographs

Quickflow, as determined by the PHS method, was roughly analogous to the rainwater end-member of CHS. Baseflow by PHS was roughly analogous to the other CHS end-members combined. Results indicated a high level of consistency between the methods for some storms, such as the February 2011 storm shown in Figure 2. However, other storms, such as the September 2010 storm shown in Figure 3, showed differing results for quickflow by PHS and rainwater by CHS. The variability may have resulted from differing assumptions made about baseflow and storm flow in the LCP. By the graphic method, quickflow was determined by discharge timescale, whereas by the chemical method, the storm flow contribution was determined by how closely the stream water chemistry mimics rainwater. In the case of the September 2010 storm event, the large variation in the methods was likely caused by the very large rainfall volume on very dry conditions. The initial rainfall infiltrated and subsequent rainfall during the storm event was interpreted as baseflow by the physical method (because it was interflowing to the stream as baseflow typically does) but as quickflow/rainwater by the chemical method (because its residence time was short,

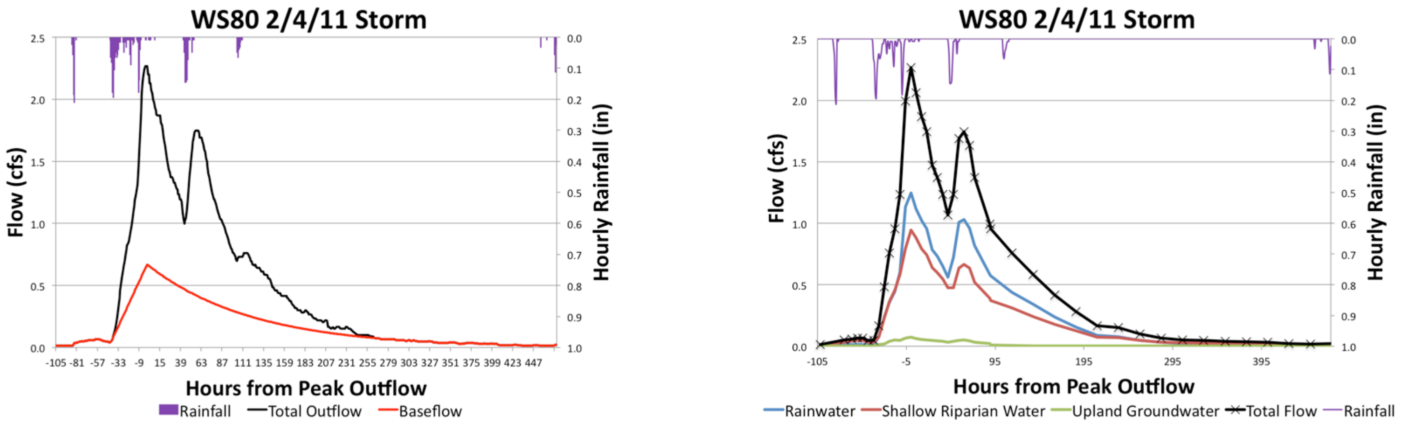

Figure 2. Physical Hydrograph Separation (left) and Chemical Hydrograph Separation (right) for the 2/4/2011 storm event. Baseflow from PHS is compared with the sum of shallow riparian water and upland groundwater from CHS.

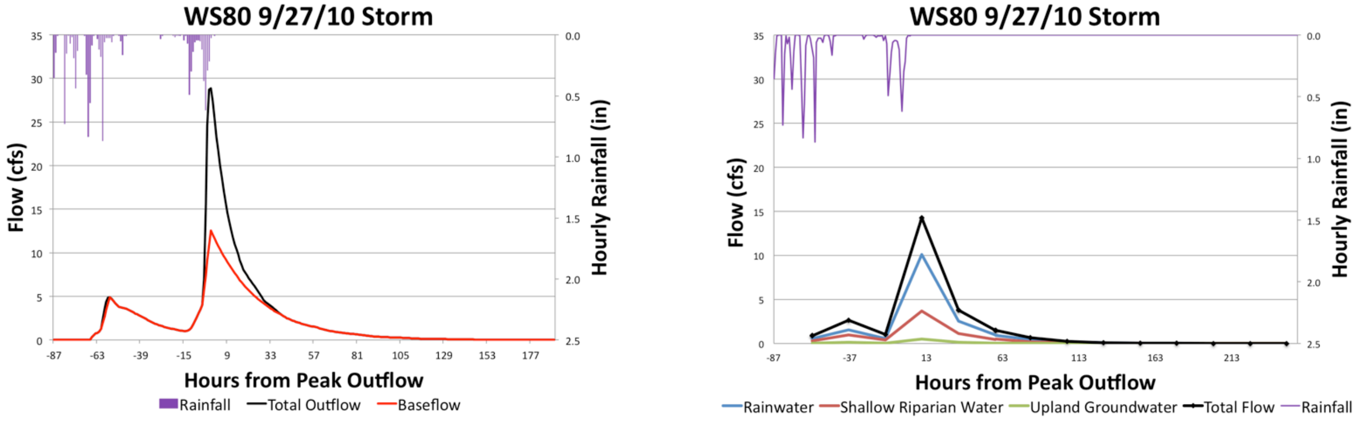

Figure 3. Physical Hydrograph Separation (left) and Chemical Hydrograph Separation (right) for the 9/27/2010 storm event.

and thus its chemistry was like rainwater). These results illustrated the complexity of runoff production dynamics in LCP watersheds and suggest that using parallel methods provides a more nuanced understanding of hydrological processes.

Implementing Water Chemistry Analysis

Our findings indicated that analysis of natural water chemistry can provide information about hydrological processes that physical approaches alone cannot supply. For a fuller understanding of water resource issues at a site, we recommend supplementing traditional physical hydrological studies with limited water chemistry analysis.

EMMA-based chemical hydrograph separation is a cumbersome process, but our results suggest that a streamlined approach is possible in order to do a relatively rapid assessment of a watershed. The following recommendations form the procedures for such an approach. In lowland watersheds, the water table is shallow, even in dry conditions, so the following piezometers can be installed by hand-augering:

- An upland piezometer, collecting groundwater from 3-5 m below ground surface (bgs).
- A riparian piezometer, collecting groundwater from 2-3 m bgs.
- A streambed piezometer, collecting groundwater from 1-2 m bgs, or above the argillic horizon, if present.
- A streambed piezometer, collecting groundwater from 3-5 m bgs.
- A streambed stilling well.

Stage height measurements are needed, which can be recorded by a data logger (Solinst Canada Ltd., Georgetown, ON) in the streambed stilling well. Our results show the importance of assessing unsaturated-zone soilwater, which is accomplished using inexpensive suction lysimeters. Rainwater can be easily collected in manual rain gauges. For rough estimates, daily streamwater samples may be adequate for profiling storm-event stream chemistry.

Water samples could be sent to a private or academic laboratory for analysis. *In situ* analysis of some values, such as chloride and conductivity, may be feasible with modern field equipment.

Statistical analyses can be performed in free, open-source software *R* (www.r-project.org), EMMA can be performed in the freely available website *WolframAlpha* (www.wolframalpha.com), and data can be compiled and hydrographs can be created in free, open-source software *OpenOffice.org* (www.openoffice.org).

It is our belief that a rough assessment of a site, using the above recommendations, can offer significant information about storm-event runoff at a site pending development in less than a year. The results can help to inform the specific stormwater practices implemented during development to manage stormwater quantity and quality issues.

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