Running title: Long-term data from Walker Branch Watershed

Long-term hydrological, biogeochemical, and climatological data from Walker Branch Watershed, east Tennessee, USA

Natalie A. Griffiths[1*] and Patrick J. Mulholland[1#]

[1]Climate Change Science Institute and Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA 37831

*Corresponding author:

Natalie A. Griffiths

E-mail: griffithsna@ornl.gov

Phone: (865) 576-3457

[#]Deceased. PJM was instrumental in sustaining the collection of these datasets for nearly 3 decades. In addition to leading data collection efforts, Pat archived the data annually and wrote the original meta-data files; these files formed the basis of this Data Note.

Abstract

In 1967, the original Walker Branch Watershed (WBW) project was established to study elemental cycling and mass balances in a relatively unimpacted watershed. Over the next 50+ years, findings from additional experimental studies and long-term observations on WBW advanced understanding of catchment hydrology, biogeochemistry, and ecology and established WBW as a seminal site for catchment science. The 97.5-ha WBW is located in east Tennessee, USA, on the U.S. Department of Energy's Oak Ridge Reservation. Vegetation on the watershed is characteristic of an eastern deciduous, second-growth forest. The watershed is divided into two subcatchments: the West Fork (38.4 ha) and the East Fork (59.1 ha). Headwater streams draining these subcatchments are fed by multiple springs, and thus flow is perennial. Stream water is high in base cations due to weathering of dolomite bedrock and nutrient concentrations are low. Long-term observations of climate, hydrology, and biogeochemistry include daily (1969-2014) and 15-min (1994-2014) stream discharge and annual runoff (1969-2014); hourly, daily, and annual rainfall (1969-2012); daily climate and soil temperature (1993-2010); and weekly stream water chemistry (1989-2013). These long-term datasets are publicly available on the WBW website (https://walkerbranch.ornl.gov/long-term-data/). While collection of these data has ceased, related long-term measurements continue through the National Ecological Observatory Network (NEON), where WBW is the core terrestrial and aquatic site in the Appalachian and Cumberland

Plateau region (NEON's Domain 7) of the United States. These long-term datasets have been and will continue to be important in evaluating the influence of climatic and environmental drivers on catchment processes.

Key Words: long-term data; stream discharge; rainfall; water chemistry; research catchment; southeastern US.

Introduction

For over a century, observational and experimental studies at dedicated research catchments have played an important role in advancing the fields of watershed hydrology and biogeochemistry (McGuire & Likens, 2011). The first research catchments established in the United States investigated the effects of forestry and agriculture on water budgets. Subsequently, there was an interest in understanding catchment-scale elemental dynamics (with a specific focus on water quality and pollution), and this line of inquiry led to the development of the Walker Branch Watershed (WBW) project in 1967 (Curlin & Nelson, 1968). The WBW project initially focused on applying a watershed-scale budget approach to studying water quality in a relatively unimpacted, forested catchment in east Tennessee, USA (Curlin & Nelson, 1968). Over the next 50+ years, the many foundational studies on catchment hydrology, biogeochemistry, and ecology at WBW solidified this watershed as a seminal research catchment. Some of these notable studies included a synthesis of land-use history (Dale, Mann, Olson, Johnson, & Dearstone, 1990), an extensive characterization of atmospheric deposition (Lindberg, Lovett, Richter, & Johnson, 1986; Lindberg, Turner, Meyers, Taylor, & Schroeder, 1991), assessments of forest biogeochemical cycling (Garten, 1993; Johnson & Todd, 1990; Trettin, Johnson, & Todd, 1999; Van Hook, Harris, & Henderson, 1977), the first *in situ* measurements of the nutrient spiraling technique in streams (Mulholland, Elwood, Newbold, Ferren, & Webster, 1985; Newbold, Elwood, O'Neill, & Shelton, 1983; Newbold, Elwood, O'Neill, & Van Winkle, 1981; Newbold, O'Neill, Elwood, & Van Winkle, 1982), analyses that identified the importance of in-stream processes in regulating stream water nutrient concentrations (Lutz, Mulholland, & Bernhardt, 2012; Mulholland, 1992; Mulholland, 2004), application of whole-stream nitrogen (N) stable isotope releases to investigate ecosystem N cycling (Mulholland et al., 2000a; Mulholland et al., 2000b), investigations of hillslope hydrogeochemistry (Jardine, Wilson, Luxmoore, & McCarthy, 1989; Jardine, Wilson, McCarthy, Luxmoore, & Taylor, 1990; Mulholland, Wilson, & Jardine, 1990; Wilson, Jardine, Luxmoore, & Jones, 1990), landscape-scale assessments of CO_2 and water vapor exchange (Baldocchi, 1997; Greco & Baldocchi, 1996; Wilson & Baldocchi, 2000; Wilson, Hanson, & Baldocchi, 2000; Wilson, Hanson, Mulholland, Baldocchi, & Wullschleger, 2001), examination of long-term terrestrial vegetation dynamics (Kardol, Todd, Hanson, & Mulholland, 2010), utilization of a large-scale experiment to examine responses of varying precipitation on terrestrial vegetation (Hanson, Todd, & Amthor, 2001; Hanson, Todd, & Huston, 2003; Wullschleger & Hanson, 2006), and examination of watershed-scale carbon cycling using a ^{14}C tracer (Cisneros-Dozal, Trumbore, & Hanson, 2006; Fröberg et al., 2007; Joslin, Gaudinski, Torn, Riley, & Hanson, 2006). Throughout this rich 50+ year history of research in WBW, long-term climatic, hydrological, and biogeochemical datasets were collected to investigate temporal patterns and to support focused research projects. In this Data Note, we describe four core datasets that were collected in WBW and its two subcatchments (West and East Forks): climate and soil temperature data (1993-2010), rainfall (1969-2012), stream discharge (1969-2012 for the East Fork, 1969-2014 for the West Fork), and stream water chemistry (1995-2013 for the East Fork, 1989-2013 for the West Fork).

Watershed Description

Walker Branch Watershed is a 97.5 ha research catchment in east Tennessee, USA (35°57'31"N, 84°16'46"W), on the U.S. Department of Energy's Oak Ridge Reservation, and within the Ridge and Valley Physiographic Province (Figure 1). Walker Branch Watershed is part of the larger Clinch River Watershed which ultimately drains into the Mississippi River.

Vegetation on the watershed is characteristic of an eastern deciduous secondary forest (primarily hickory, chestnut oak, white oak, red maple, sourwood, blackgum, yellow poplar, shortleaf pine, and Virginia pine) (Dale et al., 1990; Grigal & Goldstein, 1971; Kardol et al., 2010). The watershed is underlain by bedrock (Knox Dolomite) with soils (primarily Ultisols) that are deep (>2 m), highly weathered, acidic, and cherty (cryptocrystalline sedimentary rock) (Johnson, 1989). The climate is typical of the humid southern Appalachian region, with a mean annual temperature of 14.5 ºC and mean annual rainfall of 135 cm (Curlin & Nelson, 1968). However, temperature and rainfall patterns have changed over time; over a 20-year period (1989-2008), mean annual air temperature increased by ~1.0 ºC and rainfall decreased by 20% (Lutz et al., 2012). The majority of precipitation in the region falls as rain (Curlin & Nelson, 1968). Elevation ranges from 351 m asl on the watershed ridges to 265 m asl in the valley.

There are two subcatchments of WBW: the West Fork (38.4 ha) and the East Fork (59.1 ha). The perennially flowing streams draining the East and West Fork subcatchments are fed by multiple springs (Johnson, 1989). The 97.5-ha watershed is delineated at the confluence of these two headwater streams (Figure 1). It has been estimated that approximately 30% of baseflow in the East Fork is exported to the West Fork via the interbasin transfer of groundwater (Luxmoore & Huff, 1989). Approximately half of the ~760-m long East Fork stream is subterranean (Sheppard, Henderson, Grizzard, & Heath, 1973). The streams are characterized by pool-riffle sequences with some small cascades. Areas of exposed siliceous dolomite are present in the streams (Johnson, 1989). Otherwise, the benthos is comprised of sediments that are primarily residual chert and organic matter that accumulates in pools and behind debris dams (Johnson, 1989). Stream water is high in base cations due to weathering of the dolomite bedrock (Mulholland, 1992; Mulholland, 2004). Dissolved organic carbon and nutrient (nitrate, ammonium, soluble reactive phosphorus) concentrations are low (Lutz et al., 2012; Mulholland, 1992; Mulholland, 2004).

Methods

Climate and Soil Temperature

Climate data were collected hourly from an instrumented meteorological tower (Figure 1) and soil temperature was measured hourly at multiple locations surrounding the tower from 1993 through 2010 (Mulholland & Griffiths, 2016a). These data were initially collected as part of the Throughfall Displacement Experiment from the ambient plot (Hanson, Todd, Riggs, Wolfe, & O'Neill, 2001). The following parameters were measured above the canopy: irradiance (pyranometer sensor, LiCor LI-200SA), photosynthetic photon flux density (quantum sensor, LiCor LI-191SA), relative humidity (hygrometer, Model MP-100, Rotronics Instrument Corporation), rainfall (tipping bucket rain gauge), and wind speed (anemometer). These parameters were measured in a nearby clearing from 1993-1997 and then these instruments were added to the meteorological tower in 1998. Sub-canopy air temperature was measured ~1 m above the soil in a location shielded from direct solar radiation, and soil temperature (15 cm depth) was measured at 4 locations near the tower; both air and soil temperature were measured with thermistors (LiCor).

Rainfall

Rainfall was measured from 1969 through 2012 (Mulholland & Griffiths, 2016b). The methodology changed slightly over the 44-year record. From 1969-1979, rainfall was measured at five rain gauges that were distributed along the edge of the watershed, with one of these rain gauges at the ridge separating the East and West Fork subcatchments (Figure 1). Rainfall was measured at 5-minute intervals with a sensitivity of ± 2.5 mm (Fisher and Porter model 1548 punched-tape weighing recorder). From 1980 through 1982, data from WBW were not available, so rainfall data from the National Oceanic and Atmospheric Administration Atmospheric Turbulence and Diffusion Division laboratory in the nearby city of Oak Ridge were used. After 1983, rainfall was measured at 2 of the 5 WBW rain gauges, although data from additional rain gauges across the Oak Ridge Reservation were used when there were gaps in the WBW rainfall data record. Rainfall data were recorded hourly with a sensitivity of ± 0.25 mm from 1983 through 1998 (8-day weighing bucket strip chart recorder) and ± 0.1 mm from 1998 through 2012 (Telog electronic tipping bucket recorder).

Stream Discharge

Stream discharge was measured in the East Fork from 1969 through 2012 and in the West Fork from 1969 through 2014 (Mulholland & Griffiths, 2016c). A 120° V-notch weir was constructed at each subcatchment outlet in 1967 (Curlin & Nelson, 1968) (Figure 1). Starting in 1969, water level was measured in a stilling well with a punched-tape water-level recorder (Fisher and Porter model 1542) every 5 (until 1989) or 15 minutes (until 1999) at a ± 0.3 mm resolution. Beginning in 1999, water level was measured electronically at 15-min intervals (Stevens Type A/F encoder [1999-2010]; Campbell Compact Bubble Water Level Sensor model CS471 [2011-2014], accuracy ± 0.01 ft). Recorded data were verified at least monthly with a manual hook gauge measurement. Discharge was calculated from water level using the following equation: Discharge (L/s) = 125.37 × (water level in feet)$^{2.449}$. Uncertainty in the discharge estimate was ± 5% at flows <4 L/s and ± 0.5% at flows >125 L/s. Discharge was estimated up to

1,180 L/s using the V-notch weir equation, and a sharp-crested rectangular cross-section above the V-notch allowed for discharge to be estimated up to 1,860 L/s.

During logger malfunctions in one stream, discharge was sometimes calculated from a regression between the East and West Fork water levels. Other gap-filling methods were occasionally employed over the discharge record (Mulholland & Griffiths, 2016c). Annual runoff was calculated for each subcatchment using mean annual discharge and subcatchment area. Annual runoff was estimated for the entire watershed by summing annual runoff from both subcatchments.

Stream Water Chemistry

Water samples were collected weekly for chemistry analyses from the West Fork (1989 through 2013) and the East Fork (1995 through 2013) (Mulholland & Griffiths, 2016d). The following parameters were included in the stream water chemistry datasets: water level in the stilling well and stream discharge, water temperature, specific conductivity, pH, alkalinity, and dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), ammonium-N, nitrate+nitrite-N, total dissolved nitrogen (TDN), anion (chloride and sulfate), and cation and trace metal (calcium, magnesium, sodium, potassium, iron, manganese, silicon, aluminum, barium, cadmium, nickel, lead, strontium, zinc, copper, molybdenum) concentrations.

Weekly water samples were collected between 9:00 and 12:00 EST, usually on Tuesdays. The West Fork water samples were collected ~60 m upstream of the weir and the East Fork samples were collected ~20 m downstream of the weir. Water temperature and specific conductivity were measured in the field using a hand-held probe (ORION Model 122 probe until

July 2007, YSI Model 30 probe after July 2007) and water level in the stilling well was recorded at the time of sampling. Within an hour of collection, water samples were analyzed or processed (filtered) and preserved. pH was measured immediately on unfiltered samples using a benchtop pH meter. Unfiltered alkalinity samples were refrigerated and analyzed within 3 months of collection via titration (0.01 N HCl to a pH of 4.5). Water for solute analyses was filtered (0.45-µm pore size, Nuclepore polycarbonate filters) prior to preservation. After filtration, samples for nutrients (N and P) were frozen, samples for DOC were acidified (2 drops of 6 N HCl) and refrigerated, samples for anions were refrigerated, and samples for cations and trace metals were acidified (0.2% HNO_3) and stored at room temperature until analysis. Spectrophotometry was used for analysis of ammonium-N (phenate colorimetry), nitrate+nitrite-N (Cu-Cd reduction followed by azo dye colorimetry), TDN (alkaline persulfate digestion [to May 1996] or UV oxidation [to April 2000] followed by azo dye colorimetry), SRP (ascorbic acid colorimetry), and TDP (persulfate oxidation followed by ascorbic acid colorimetry). DOC was analyzed via high-temperature combustion (TOC-TN analyzer) as was TDN (after April 2000). Anions were analyzed via ion chromatography (at Oak Ridge National Laboratory's [ORNL] Analytical Chemistry Division prior to January 1999 and at ORNL's Environmental Sciences Division after January 1999) and cations and trace metals were analyzed via inductively coupled plasma emission spectroscopy (at the University of Georgia prior to 1996 and at ORNL/Y-12 National Security Complex after 1996). While the analytical methods were consistent over time (except for TDN), instrumentation changed as laboratory equipment was upgraded. Therefore, detection limits also changed over time; these detection limits (when known) are reported in the metadata file (Mulholland & Griffiths, 2016d). There are some gaps in the dataset for certain analytes. DOC samples were not collected from 1997 through 2002, trace metal concentration data are generally absent from 1989 through 1991 and again from 1998 through 2002, and anion and cation concentration data are absent for most of 1990.

Complimentary Datasets

There are several publicly available hydrological, biogeochemical, and ecological datasets that are not part of the four core WBW datasets described here, but together they can complement and enhance understanding of catchment processes in WBW. From 1980-2011, WBW participated in the National Atmospheric Deposition Program (NADP; http://nadp.slh.wisc.edu/data/) National Trends Network (site ID: TN00), with weekly samples collected for wet precipitation chemistry. Precipitation chemistry samples were also collected on an event basis through NADP's Atmospheric Integrated Research Monitoring Network from 1992-2019.

Vegetation inventories on 306 permanent plots established on WBW were conducted 9 times over a span of 40 years (1967, 1970, 1973, 1979, 1983, 1987, 1991, 1997, 2006) (Grigal & Goldstein, 1971; Huston, Johnson, Todd, Curlin, & Harris, 2013). The permanent plots were located in one of four vegetation types (chestnut oak, oak-hickory, pine, and yellow poplar). Trees within the plots were tagged and diameter at breast height was recorded on each date. These data are archived online (https://doi.org/10.3334/ORNLDAAC/819) and are summarized in Kardol et al., (2010). Micrometeorological measurements of CO_2 fluxes were measured from 1995-1999 and are part of the AmeriFlux Network (https://doi.org/10.17190/AMF/1246109). Benthic samples for stream macroinvertebrate community characterization were collected ~30 m downstream of the East and West Fork confluence each spring (April) beginning in 2000 (Matson et al., in review). There are many other datasets from experimental and observational studies on WBW that are primarily reported in publications (i.e., in figures and tables), but some datasets are archived (e.g., Griffiths & Johnson, 2018; Griffiths & Tiegs, 2016).

Due in part to the rich ecological knowledge and wealth of data collected in WBW, the watershed was selected as one of the core terrestrial and aquatic sites in the National Ecological Observatory Network (NEON). Physical, chemical, and biological data collection in WBW and the surrounding Oak Ridge Reservation began in 2015-2017 and these measurements are expected to continue for 30 years (Keller, Schimel, Hargrove, & Hoffman, 2008). These data are available on the NEON data portal (https://data.neonscience.org/home).

Data

Data Description

The four long-term datasets described here are publicly available via the WBW website (https://walkerbranch.ornl.gov/long-term-data/) at https://doi.org/10.3334/CDIAC/ornlsfa.006; https://doi.org/10.3334/CDIAC/ornlsfa.007; https://doi.org/10.3334/CDIAC/ornlsfa.008; https://doi.org/10.3334/CDIAC/ornlsfa.009. All datasets are accompanied by associated metadata files which describe the datasets, as well as the study site and methodology. Climate and soil temperature data from 1993-2010 are provided in one dataset (Mulholland & Griffiths, 2016a). Most parameters are reported as daily means; however, the minimum and maximum soil and air temperatures and relative humidity (based on hourly data) are also reported, as are the integrated daily irradiance, integrated daily photosynthetic photon flux density, and total daily rainfall. The rainfall data are described in three separate datasets that report rainfall in total hourly, total daily, and total annual amounts from 1969-2012 (Mulholland & Griffiths, 2016b). Similarly, the discharge data include three separate datasets. Mean daily discharge and annual runoff are reported from 1969 through 2012 (East Fork) and 1969 through 2014 (West Fork), while 15-minute discharge data are reported beginning in 1994 (Mulholland & Griffiths, 2016c). Weekly stream water chemistry data are reported in two datasets: one for the West Fork (1989-2013) and one for the East Fork (1995-2013) (Mulholland & Griffiths, 2016d). Temporal patterns in total daily rainfall, mean daily discharge, mean daily air temperature, and weekly stream water nitrate concentrations are shown in Figure 2 to provide an example of measured parameters from each of the four datasets described in this Data Note.

Data Contributors

A major challenge of curating and archiving datasets that span multiple decades (and scientific careers) is the loss of institutional knowledge, including names of all scientific and technical staff that contributed to the collection of these data. Those who contributed to the four datasets described here are listed based on personal knowledge, discussions with staff members, and from publications and reports. However, it is likely that some individuals are not listed below and we regret these unintended omissions.

The climate and soil temperature dataset was initiated by the Throughfall Displacement Experiment research team (P.J. Hanson, J.S. Riggs, and D.E. Todd) and collection and archiving of this dataset was led by P.J. Hanson, P.J. Mulholland, J.S. Riggs, and D.E. Todd. Collection of rainfall and stream discharge data was led and executed by multiple scientists including J.W. Curlin, T. Grizzard, G.S. Henderson, D.D. Huff, P.J. Mulholland, and D.J. Nelson, and many technical staff including D.J. Brice and D.E. Todd. Collection of stream water chemistry data was initiated by P.J. Mulholland with technical assistance from D.J. Brice, B.K. Konetsky, B. Lu, M.K. McCracken, J.R. Phillips, and R.V. Wilkerson along with many students and

postdoctoral research associates. Collection of all four datasets was continued by N.A. Griffiths beginning in autumn 2010 until the end date of each dataset. N.A. Griffiths also curated the final datasets and compiled the metadata files (Mulholland & Griffiths, 2016abcd) with assistance from L.A. Hook. Funding that supported the long-term studies in WBW was primarily from the U.S. Department of Energy, Office of Science, Biological and Environmental Research program (and predecessor programs), and from the National Science Foundation (including the U.S. International Biological Program, Eastern Deciduous Forest Biome).

Long-term Data to Advance Understanding of Catchment Hydrological and Biogeochemical Dynamics

Research in WBW has made significant contributions to the understanding of catchment hydrology, biogeochemistry, and ecology, and the datasets described here have been critical to many of these scientific advancements. For instance, analysis of these datasets revealed changes in solute concentrations and fluxes over a 20-year period due to a decrease in catchment runoff and a shifting importance of hydrologic pathways that contribute to streamflow (Lutz et al., 2012). These datasets were also important in understanding stream ecosystem responses to a disturbance event, specifically, a spring freeze that damaged newly developed leaves and prolonged the period of an open canopy/increased light availability to the stream (Mulholland, Roberts, Hill, & Smith, 2009). Many other studies in WBW, both observational and experimental, have utilized parts of these datasets in their analyses, including studies examining the controls on stream metabolism (Roberts, Mulholland, & Hill, 2007), nutrient uptake rates (Roberts & Mulholland, 2007), and solute concentrations (Mulholland, 2004; Mulholland & Hill, 1997).

While the datasets described here have primarily been used to understand patterns and drivers of hydrological, biogeochemical, and ecological processes within WBW, these parameters (i.e., climate, rainfall, discharge, stream water chemistry) are often measured in other research catchments and thus these data lend themselves to multi-watershed analyses. For example, WBW was included in a synthesis that investigated the controls on N inputs and losses across 15 catchments (Kane et al., 2008). It is anticipated these long-term datasets from WBW, especially in combination NEON data, will be used in future cross-watershed studies to examine the influence of climatic and environmental drivers on catchment processes at regional, continental, and global scales.

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Figure Legend

Figure 1 – Map of the 97.5-ha Walker Branch Watershed (with West Fork and East Fork subcatchments also delineated) and photos (from June 2008) of hydrologic infrastructure and a stream water chemistry sampling site. The datasets described in this paper were collected at the meteorological tower, rain gauges, stream weirs, and stream water chemistry sampling sites shown on the topographic map of Walker Branch Watershed (left image). The location of Walker Branch Watershed within the southeastern United States is also shown (left image inset). Photos show the West Fork weir and weir hut (top right image) and the stream chemistry sampling site (bottom right image). Photo credit: Jason Richards/Oak Ridge National Laboratory, U.S. Department of Energy.

Figure 2 – Temporal patterns in total daily rainfall (mm), mean daily discharge (L/s), mean daily air temperature (°C), and weekly stream water nitrate concentration (μg N/L) in Walker Branch Watershed. Discharge and stream water nitrate concentration data are from the West Fork of Walker Branch. Nitrate concentrations were below 120 μg N/L except for one date (12/8/1998) when nitrate was 297 μg N/L (datapoint not shown on figure).