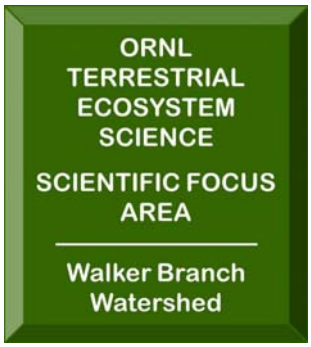

Walker Branch Watershed: Weekly Stream Water Chemistry

Summary:

This data set reports weekly stream water chemistry in the West and East Forks of Walker Branch Watershed (WBW). The long-term Walker Branch stream chemistry monitoring is intended to provide data on watershed output of chemicals via streamflow and long-term changes in stream chemical composition. This data set contains two data files of stream water chemistry collected at weekly time intervals from 1989 through 2013. Weekly sampling of stream water started in 1989 in the West Fork and in 1995 in the East Fork. Measured parameters include water level at the weir 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.

Data Citation:

Cite this data set as follows:

Mulholland, P.J., and N.A. Griffiths. 2016. Walker Branch Watershed: Weekly Stream Water Chemistry. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, U.S.A.
http://dx.doi.org/10.3334/CDIAC/ornlsfa.009

Acknowledgement of Sponsor for Terrestrial Ecosystem Science - Scientific Focus Area (TES SFA):

This research was sponsored by the Terrestrial Ecosystem Science Program, Office of Biological and Environmental Research within the U.S. Department of Energy's Office of Science.

Data and Documentation Access:

For public access to WBW data please visit the ORNL TES-SFA Web Site:
http://tes-sfa.ornl.gov/

Walker Branch Watershed website: http://walkerbranch.ornl.gov/

Long-term monitoring of WBW is continuing through the National Ecological Observatory Network (NEON), and data are available from the NEON website: http://www.neonscience.org/.

Publications related to this data set:

Curlin, J.W., and D.J. Nelson. 1968. Walker Branch Watershed project: Objectives, facilities, and ecological characteristics. ORNL/TM-2271. Oak Ridge National Laboratory, Oak Ridge, TN.

Lutz, B.D., P.J. Mulholland, and E.S. Bernhardt. 2012. Long-term data reveal patterns and controls on stream water chemistry in a forested stream: Walker Branch, Tennessee. Ecological Monographs 82:367-387.

Mulholland, P.J. 1992. Regulation of nutrient concentrations in a temperate forest stream: roles of upland, riparian, and instream processes. Limnology and Oceanography 37:1512-1526.

Mulholland, P.J. 1993. Hydrometric and stream chemistry evidence of three storm flowpaths in Walker Branch Watershed. Journal of Hydrology 151:291-316.

Mulholland, P.J., and W.R. Hill. 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. Water Resources Research 33:1297-1306.

Mulholland, P.J. 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. Biogeochemistry 70:403-426.

Data Policy - Sharing, Access, and Use Recommendations: ORNL TES-SFA Data Policy - Data Policy and Fair-Use Statement

Related Data Sets: Historical climate, precipitation, and stream discharge data are available at http://tes-sfa.ornl.gov/. Environmental data from WBW are also available from the NEON website: http://www.neonscience.org/.

Walker Branch Watershed (WBW) Project Description:

Walker Branch Watershed (WBW) is a forested watershed on the Oak Ridge Reservation and has been the site of long-term environmental research since the 1960s. Hydrological, biogeochemical, and ecological studies in WBW have made important contributions to our understanding of the effects of changes in atmospheric deposition and climate variability and change in this region (see http://walkerbranch.ornl.gov/publications.shtml for complete list of publications).

Objectives of the WBW long-term observations have been to:

1. Quantify responses of an eastern upland oak forest ecosystem to inter-annual and long-term variations in climate and atmospheric deposition of sulfur and nitrogen, and
2. Provide integrated, long-term data on climate, forest vegetation, soil chemistry, and hydrologic and chemical fluxes at the catchment scale to support other focused research projects on the Oak Ridge Reservation and elsewhere in the region.

Table of Contents:

1. Data Set Overview:

This data set reports the weekly stream water chemistry in the West and East Forks of Walker Branch Watershed from 1989-2013. Measured parameters include water level at the weir 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.

2. Data Characteristics:

Spatial Coverage:

This research was conducted in Walker Branch Watershed. West Fork water samples were collected at a site approximately 60 m upstream from the weir. East Fork water samples were collected approximately 20 m downstream from the weir (Fig. 1 shows locations of the weirs).

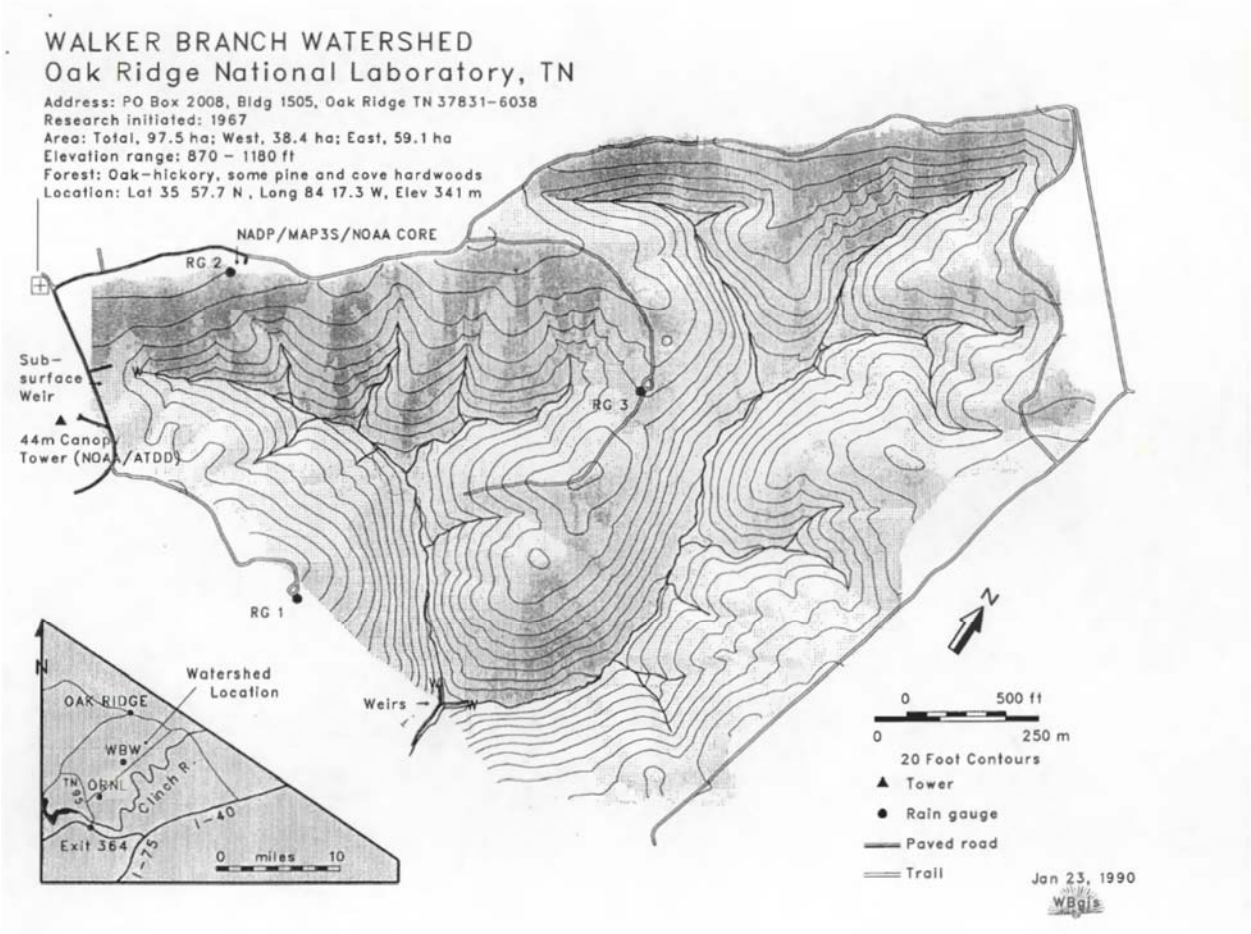

Figure 1 – Topographic map of Walker Branch Watershed showing the locations of weirs. The West Fork is on the left and the East Fork is on the right. West Fork water samples were collected approximately 60 m upstream from the weir. East Fork water samples were collected approximately 20 m downstream from the weir.

Site boundaries: Latitude and longitude given in decimal degrees. Source Google Earth.

Site (Region)	Longitude	Latitude	Elevation (meters amsl)	Geodetic Datum
West Fork weir pool of Walker Branch Watershed	-84.27951	35.95879	265	WGS84
East Fork weir pool of Walker Branch Watershed	-84.27922	35.95869	265	WGS84

Temporal Coverage:

Time period: The data set covers the period from January 3, 1989 to October 29, 2013 for the West Fork, and from January 4, 1995 to October 29, 2013 for the East Fork.

Data File Description:

All of the data are contained in 2 comma separated (*.csv) files. Missing values are represented by -9999.

- File #1: WBW_west_stream_chemistry.csv
- File #2: WBW_east_stream_chemistry.csv

Data Dictionary:

File #1: WBW_west_stream_chemistry.csv

Column	Heading	Units/ Format	Description	Measurement Method
1	DATE	YYYYMMDD	Measurement date.	
2	EF_LEVEL	ft	Stage height (water level) measured at the weir at the time of sample collection.	Water level recorder or bubble level sensor (see Methods).
3	EF_DISCHARGE	L/s	Stream discharge for the East Fork of Walker Branch at the time of sample collection.	Calculated discharge based on the dimensions of the v-notch weir.
4	TEMP	°C	*In situ* stream water temperature measured at time of sample collection.	Hand-held temperature and conductivity probe.
5	SP_COND	µS/cm	*In situ* specific conductivity measured at the time of sample collection.	Hand-held temperature and conductivity probe.
6	pH		pH of unfiltered water sample.	Benchtop pH meter.
7	ALK	mg $CaCO_3$/L	Alkalinity of unfiltered water sample.	Titration with 0.01N HCl to a pH of 4.5.
8	DOC_CONC	mg/L	Dissolved organic carbon (DOC) concentration.	High temperature combustion using an OI model 700 Total Organic Carbon analyzer prior to March 1992 and a Shimadzu Model 5000 Total Organic Carbon analyzer after March 1992.
9	SRP_CONC	µg P/L	Soluble reactive phosphorus (SRP) concentration.	Ascorbic acid method (APHA 1995) using 10 cm pathlength spectrophotometric cell.
10	TDP_CONC	µg P/L	Total dissolved phosphorus (TDP) concentration.	Persulfate oxidation followed by the ascorbic acid method (APHA 1995).
11	NH4_N_CONC	µg N/L	Ammonium-N concentration.	Automated phenate colorimetry (APHA 1995) using Bran Luebbe TRAACS autoanalyzer prior to July 1999 and Bran Luebbe AAIII autoanalyzer after July 1999.
12	NO3_N_CONC	µg N/L	Nitrate+nitrite-N concentration.	Automated Cu-Cd reduction followed by azo dye colorimetry (APHA 1995) using Bran Luebbe TRAACS autoanalyzer prior to July 1999 and Bran Luebbe AAIII autoanalyzer after July 1999.

13	TDN_CONC	µg N/L	Total dissolved nitrogen (TDN) concentration.	Alkaline persulfate digestion followed by nitrate analysis prior to May 1996 (APHA 1995); UV oxidation followed by nitrate analysis between May 1996 and April 2000; High temperature combustion (Shimadzu TNM-1) after April 2000.
14	CL_CONC	mg/L	Chloride concentration.	Ion chromatography (APHA 1995).
15	SO4_CONC	mg/L	Sulfate concentration.	Ion chromatography (APHA 1995).
16	CA_CONC	mg/L	Calcium concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
17	MG_CONC	mg/L	Magnesium concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
18	NA_CONC	mg/L	Sodium concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
19	K_CONC	mg/L	Potassium concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
20	K_CONC_FL		Data quality flag.	See Data Flag Table.
21	FE_CONC	mg/L	Iron concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
22	FE_CONC_FL		Data quality flag.	See Data Flag Table.
23	MN_CONC	mg/L	Manganese concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
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32	NI_CONC	mg/L	Nickle concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
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34	PB_CONC	mg/L	Lead concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
35	PB_CONC_FL		Data quality flag.	See Data Flag Table.
36	SR_CONC	mg/L	Strontium concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).
37	SR_CONC_FL		Data quality flag.	See Data Flag Table.
38	ZN_CONC	mg/L	Zinc concentration.	Inductively coupled plasma emission spectroscopy (APHA 1995).

39	ZN_CONC_FL		Data quality flag.	See Data Flag Table.
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Historical Walker Branch datasets are available at: http://tes-sfa.ornl.gov/ and information about Walker Branch Watershed is available at: http://walkerbranch.ornl.gov/. Missing data denoted as '-9999'.				

Example Data Records:

DATE,WF_LEVEL,WF_DISCHARGE,TEMP,SP_COND,PH,ALK,DOC_CONC,SRP_CONC,TDP_CONC,NH4_N_CONC,NO3_N_CONC,TDN_CONC,CL_CONC,SO4_CONC,CA_CONC,MG_CONC,NA_CONC,K_CONC,K_CONC_FL,FE_CONC,FE_CONC_FL,MN_CONC,MN_CONC_FL,SI_CONC,AL_CONC,AL_CONC_FL,BA_CONC,BA_CONC_FL,CD_CONC,CD_CONC_FL,NI_CONC,NI_CONC_FL,PB_CONC,PB_CONC_FL,SR_CONC,SR_CONC_FL,ZN_CONC,ZN_CONC_FL,CU_CONC,CU_CONC_FL,MO_CONC,MO_CONC_FL
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File #2: WBW_east_stream_chemistry.csv

Column	Heading	Units/ Format	Description	Measurement Method
1	DATE	YYYYMMDD	Measurement date.	
2	EF_LEVEL	ft	Stage height (water level) measured at the weir at the time of sample collection.	Water level recorder or bubble level sensor (see Methods).
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Historical Walker Branch datasets are available at: http://tes-sfa.ornl.gov/ and information about Walker Branch Watershed is available at: http://walkerbranch.ornl.gov/.

Missing data denoted as '-9999'.

Example Data Records:

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DATE,EF_LEVEL,EF_DISCHARGE,TEMP,SP_COND,PH,ALK,DOC_CONC,SRP_CONC,TDP_CONC,NH4_N_CONC,NO3_N_CONC,TDN_CONC,CL_CONC,SO4_CONC,CA_CONC,MG_CONC,NA_CONC,K_CONC,K_CONC_FL,FE_CONC,FE_CONC_FL,MN_CONC,MN_CONC_FL,SI_CONC,AL_CONC,AL_CONC_FL,BA_CONC,BA_CONC_FL,CD_CONC,CD_CONC_FL,NI_CONC,NI_CONC_FL,PB_CONC,PB_CONC_FL,SR_CONC,SR_CONC_FL,ZN_CONC,ZN_CONC_FL,CU_CONC,CU_CONC_FL,MO_CONC,MO_CONC_FL
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```

3. Data Application and Derivation:

The long-term stream chemistry monitoring in Walker Branch is intended to provide data on watershed output of chemicals via streamflow and long-term changes in stream chemical composition. These data were used in various publications on hydrology and biogeochemistry in Walker Branch.

4. Quality Assessment:

These data are considered at Level 2. Level 2 indicates that, in addition to the Level 1 checks, the product is a complete, externally consistent data product that has undergone interpretative and diagnostic analyses and can be shared with the public. Level 1 indicates an internally consistent data product that has been subjected to quality checks and data management procedures. Instrument calibrations were carried out following the manufacturer's instructions and analyses followed published procedures.

5. Data Acquisition Materials and Methods:

Site Description:
Walker Branch Watershed (WBW) is a 97.5 ha second-growth forest on the U.S. Department of Energy's Oak Ridge Reservation in east Tennessee, USA. There are two headwaters streams that drain the watershed: the West Fork drains 38.4 ha and the East Fork drains 59.1 ha (Curlin and Nelson 1968). The watershed is underlain by bedrock (Knox Dolomite) with deep soils, primarily Utisols. Vegetation is primarily oaks (*Quercus prinus, Quercus alba*), tulip poplar (*Liriodendron tulipifera*), red maple (*Acer rubrum*), and American beech (*Fagus grandifolia*) (Johnson 1989, Kardol et al. 2010). The climate is typical of the southern Appalachian region, with a mean annual temperature of 14.5ºC and mean annual precipitation of 135 cm (Curlin and Nelson 1968, Johnson 1989).

Water Sample Collection and Processing:
Weekly sampling of stream water started in 1989 in the West Fork and in 1995 in the East Fork. Grab samples were collected between the hours of 09:00 and 12:00 EST on Tuesdays. In some years, grab samples were collected on 1-3 additional dates of high discharge. West Fork samples were collected at a site approximately 60 m upstream from the weir. East Fork samples were collected at a site approximately 20 m downstream from the weir (Fig. 1). Water temperature and specific conductance were measured in the field using an ORION Model 122 meter until July 2007 and then a YSI Model 30 meter after July 2007. Water samples were collected and returned to the laboratory within 1 hour for processing and analysis.

In the laboratory, unfiltered samples were analyzed for pH and alkalinity. pH was measured within 1 hour (sample not equilibrated with the atmosphere) using a benchtop pH meter. Samples for alkalinity were refrigerated until analysis (within 3 months). Alkalinity was measured by titration with 0.01N HCl to a pH of 4.5. Approximately 250 mL of stream water was filtered (0.45 µm pore size, Nuclepore polycarbonate filters) within 1 hour of return from the

field for analysis of solutes. Separate filtered samples were stored for the following analyses: (1) soluble N and P concentrations (frozen), (2) dissolved organic carbon (DOC) concentrations (acidified to a pH <3 with 2 drops of 6N HCl and refrigerated), (3) Cl and SO_4 concentrations (refrigerated), and (4) major cations, metals, and Si (acidified to 0.2% HNO_3 and stored at room temperature).

Analytical Methods:
Ammonium-N: Automated phenate colorimetry (APHA 1995) using a Bran Luebbe TRAACS autoanalyzer prior to July 1999 and a Bran Luebbe AAIII autoanalyzer after July 1999.

Nitrate+nitrite-N: Automated Cu-Cd reduction followed by azo dye colorimetry (APHA 1995) using a Bran Luebbe TRAACS autoanalyzer prior to July 1999 and a Bran Luebbe AAIII autoanalyzer after July 1999.

Total Dissolved N (TDN): Alkaline persulfate digestion followed by nitrate analysis prior to May 1996 (APHA 1995); UV oxidation followed by nitrate analysis between May 1996 and April 2000; High temperature combustion (Shimadzu TNM-1) after April 2000.

Soluble Reactive Phosphorus (SRP): Ascorbic acid method (APHA 1995) using 10 cm pathlength spectrophotometric cell.

Total Dissolved Phosphorus (TDP): Persulfate oxidation followed by the ascorbic acid method (APHA 1995).

Dissolved organic carbon (DOC): High temperature combustion method using an OI model 700 Total Organic Carbon analyzer prior to March 1992 and a Shimadzu Model 5000 Total Organic Carbon analyzer after March 1992.

Cl and SO_4: Ion chromatography (APHA 1995).

Ca, Mg, Na, K, Fe, Mn, Si, Al, trace metals: Inductively coupled plasma emission spectroscopy (APHA 1995).

Detection Limits:
The following are the detection limits that were reported in the dataset. The detection limits changed over time likely due to changes in instrumentation used for analysis. Detection limits for pH, alkalinity, ammonium-N, nitrate+nitrite-N, TDN, SRP, TDP, DOC, Cl, SO_4, Ca, Mg, Na, and Si were not reported.

Solute	Detection limit and dates
K	No detection limit reported before 12/31/1996 (East and West Forks) <1 mg/L from 01/07/1997 until 12/29/2009 (East and West Forks) <2 mg/L from 01/05/2010 until 08/17/2010 (West Fork only; only one date of 01/05/2010 had a <2 mg/L detection limit for East Fork data) <1 mg/L from 08/24/2010 onwards (East and West Forks)
FE	<0.01 mg/L from 01/03/1989 until 12/30/1997 (West Fork only; no detection limit reported in East Fork during this time) <0.05 mg/L from 01/06/1998 onwards (East and West Forks)
MN	<0.001 from 01/03/1989 until 12/30/1997 (West Fork only; no detection limit reported in East Fork during this time)

	<0.005 mg/L from 01/06/1998 onwards (East and West Forks)
AL	No detection limit reported before 12/30/1997 (East and West Forks) <0.20 mg/L from 01/06/1998 onwards (East and West Forks)
BA	No detection limit reported before 08/17/2010 (East and West Forks) <0.004 mg/L first reported 08/24/2010 (East and West Forks)
CD	No detection limit reported before 04/29/2003 (East and West Forks) <0.010 mg/L from 05/06/2003 onwards (East and West Forks)
NI	No detection limit reported before 04/29/2003 (East and West Forks) <0.050 mg/L from 05/06/2003 onwards (East and West Forks)
PB	No detection limit reported before 04/29/2003 (East and West Forks) <0.100 mg/L from 05/06/2003 until 08/26/2003 (East and West Forks) <0.500 mg/L from 09/02/2003 until 12/30/2003 (West Fork only; East Fork detection limit reported as <0.100 mg/L during this time) <0.100 mg/L from 01/06/2004 onwards (East and West Forks)
SR	No detection limit reported before 04/29/2003 <0.0050 mg/L from 05/06/2003 onwards (East and West Forks)
ZN	No detection limit reported before 12/29/1998 (East and West Forks) <0.0500 mg/L from 01/05/1999 onwards (East and West Forks)
CU	No detection limit reported before 04/29/2003 (East and West Forks) <0.0200 mg/L from 05/06/2003 onwards (East and West Forks)
MO	No detection limit reported before 12/29/1998 (East and West Forks) <0.0500 mg/L from 01/05/1999 until 01/18/2005 (East and West Forks) <0.0200 mg/L from 01/25/2005 onwards (East and West Forks)

Data Flags:

Flag value	Description
V0	**Valid value**
V1	**Valid value but comprised wholly or partially of below detection limit data**
V2	Valid estimated value
V3	Valid interpolated value
V4	Valid value despite failing to meet some QC or statistical criteria
V5	Valid value but qualified because of possible contamination (e.g., pollution source, laboratory contamination source)
V6	Valid value but qualified due to non-standard sampling conditions (e.g., instrument malfunction, sample handling)
V7	**Valid value but set equal to the detection limit (DL) because the measured value was below the DL**
M1	**Missing value because no value is available**
M2	Missing value because invalidated by data originator
H1	Historical data that have not been assessed or validated

Flags used in this dataset are shown in bold above.

Data collected during periods when no detection limit (DL) was reported were flagged as ‘V1’ if a value was lower than the lowest DL reported for that solute. Detection limits were not always reported for the East Fork, so the same criteria were applied (i.e., data collected during periods when no detection limit was reported in the East Fork were flagged as ‘V1’ if a value was lower than the lowest DL reported in the West Fork for that solute). During time periods when a DL was reported, if a value was reported as lower than the DL but was not flagged as <DL, that value is also flagged as ‘V1’. Data above the detection limit were flagged as ‘V0’. Concentrations reported as <DL were presented as having a concentration at the detection limit, with a flag of ‘V7’. Missing data (either analyses were not run or water samples were not collected, the latter likely due to dry conditions) are flagged as ‘M1’.

6. References:

American Public Health Association (APHA). 1995. Standard Methods for the Examination of Water and Waste Water. 19th edition, American Public Health Association, Washington, DC.

Curlin, J. W., and D. J. Nelson. 1968. Walker Branch Watershed project: objectives, facilities, and ecological characteristics. ORNL-TM-2271. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Johnson, D. W. 1989. Site description. Pages 6-20 *in* D. W. Johnson and R. I. Van Hook (editors). Analysis of biogeochemical cycling processes in Walker Branch Watershed. Springer-Verlag, New York, New York.

Kardol, P., D. E. Todd, P. J. Hanson, and P. J. Mulholland. 2010. Long-term successional forest dynamics: species and community responses to climatic variability. Journal of Vegetation Science 21:627-642.

7. Data Access:

This data is available through the Oak Ridge National Laboratory (ORNL) Carbon Dioxide Information Analysis Center (CDIAC)

Data Archive Center:
Contact for Data Center Access Information:
E-mail: http://cdiacservices.ornl.gov/feedback.cfm