SHENANDOAH WATERSHED STUDY

SHENANDOAH NATIONAL PARK WATER QUALITY MONITORING

2016 data report

Report Submitted to:

Shenandoah National Park

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1. Overview

The Department of Environmental Sciences at the University of Virginia maintains the Shenandoah Watershed Study (SWAS) program in cooperation with Shenandoah National Park (SHEN). Over the 38-year period, 1979-2016, the SWAS program has developed and maintained a monitoring framework designed to account for the spatial and temporal variability of hydrologic and biogeochemical conditions in the watershed ecosystems of the Shenandoah National Park. The SWAS monitoring program is a component of the SHEN Natural Resource Inventory and Monitoring Program. The SWAS framework includes 15 primary study watersheds in SHEN (see Figure 1).

Monitoring for the SWAS program study watersheds includes quarterly, weekly, and more-frequent, high-runoff (episodic) sample collection for analysis of stream water composition, and discharge gauging. This data collection allows detection of biogeochemical change in SHEN watersheds and supports research to advance understanding of factors and processes that govern current conditions and determine response to stressors. Coordination with the Virginia Trout Stream Sensitivity Study (VTSSS), which conducts water sampling and analysis for mountain streams throughout western Virginia, provides regional context for SWAS program data and interpretive analysis.

The water chemistry and discharge data for SWAS study streams during the 2016 calendar year are provided separately in Excel and/or Access file formats, and this annual report provides a summary of that information. Specifically, this report provides the number of samples of different types (weekly, episodic, and quarterly) in 2016 and in previous years, comparisons of mean concentrations of key acid-base constituents in 2016 and previous years, plots of base flow and episodic acid neutralizing capacity for intensively studied streams, and plots of inter-annual variation in stream discharge. Data are available to the public via NPSTORET or available in Excel or Access database format upon request. All data reports are also available at https://irma.nps.gov/DataStore/Reference/Profile/2239135.

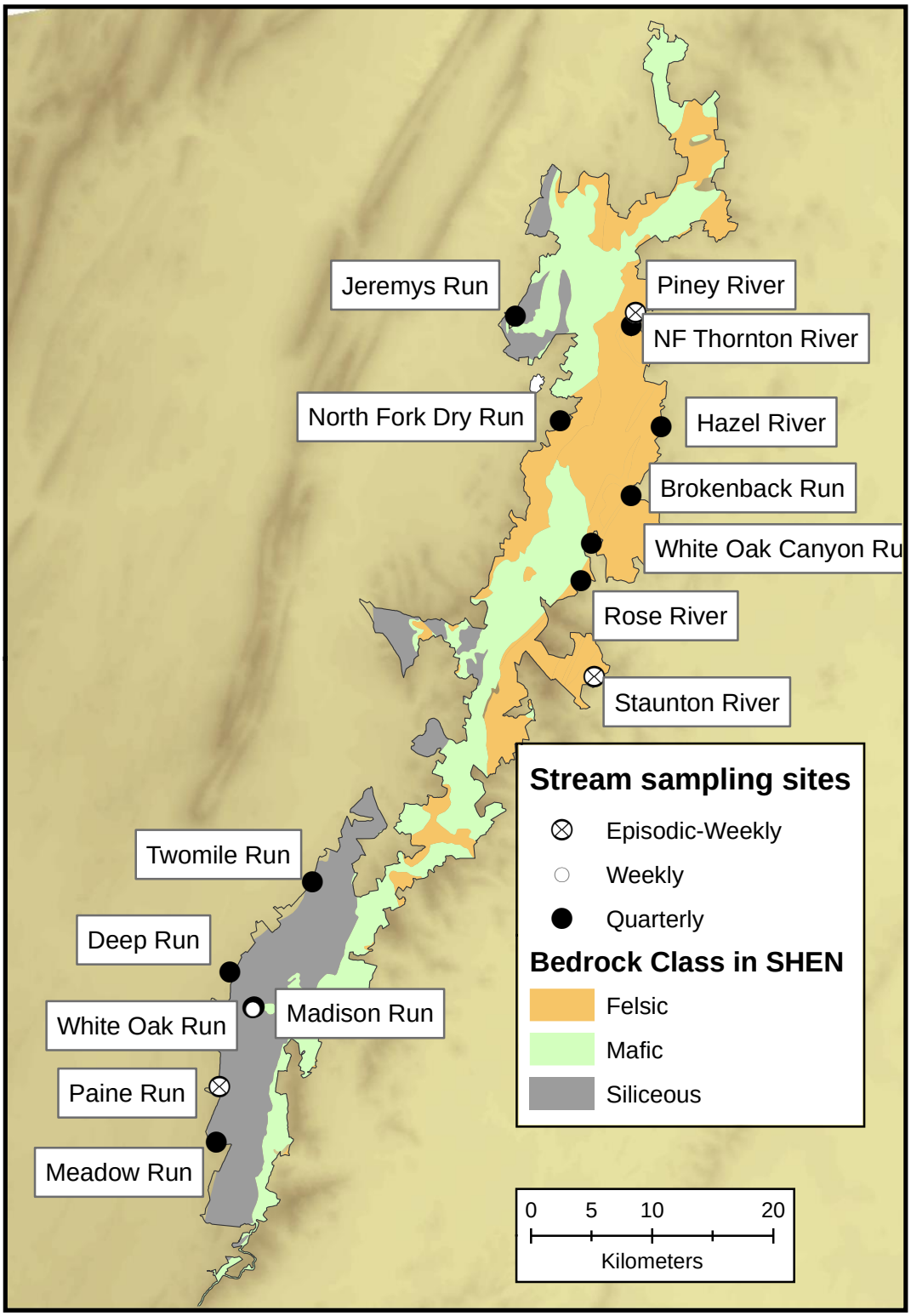

Figure 1. SWAS monitoring sites within SHEN.

Key points relating water quality to aquatic health include:

- The most extreme conditions, with respect to effects of acid-base chemistry on aquatic biota occur during episodic high-flow conditions (storm events).
- Lower acid neutralizing capacity (ANC) levels occur late fall through early spring, which is when sensitive life stages (eggs and fry) of brook trout (*Salvelinus fontainalis*) are present.

Summary/Highlights for 2016 data include:

- Nitrate concentrations which began increasing in the Piney River (PINE) watershed in 2012/2013 have begun to decline in 2015/2016, but still remain elevated compared to pre-2012. The reasons for the increase are currently unknown.
- Sum of base cation means in 2016 were lower than in previous years at all siliciclastic sites, two of the four granitic sites, and one out of five basaltic sites. The base cations are mainly derived from watershed soils, and depletion of base cations in watershed soils is a primary aspect of ecosystem harm associated with both acidic deposition and forest disturbance.
- Annual discharge was higher (mean 25%) in 2016 than the long-term mean for three currently gauged streams, Paine Run (PAIN), White Oak Run (WOR1) and PINE but 29% lower for Staunton River (STAN).
- April flows were lower than the long-term monthly mean for all sites; note the Rocky Mount Fire began during this dry period, mid-April, 2016.
- Minimum daily flows occurred in September at all sites, WOR1 recorded the lowest daily flow (0.06 cfs) followed by PAIN (1.48 cfs), PINE (2.34 cfs) and STAN (3.18 cfs).
- Maximum weekly temperatures were recorded in either July or August for each site, ranging from 21.0-21.5 ^{o}C.

Main findings from recent papers using long-term SWAS data include:

- For streams in western Virginia, from 1987 to 2011, pH has increased at a majority of sites, though acid neutralizing capacity has decreased (due to a decline in base cations) at most

sites underlain by base-poor bedrock suggesting susceptibility to episodic acidification is still a threat in these streams, *Robison et al., 2013*

- Mass balance analysis using historic discharge and chemistry data indicate watersheds in SHEN will cross over from sulfate-retaining to sulfate-releasing systems in years ranging from 2012 to 2021, implying that within the next decade sulfate stream concentrations will steadily decrease fulfilling one of the intended outcomes of the Clean Air Act Regulations. *Rice et al., 2014*

This annual report has been prepared for the Natural Resources Division at SHEN. Additional information related to the SWAS monitoring program in SHEN, including program history, design, findings, and procedures is provided in the draft *Shenandoah National Park and Shenandoah Watershed Study Water Quality Monitoring Program Protocol* and associated Standard Operating Procedure (SOP) documents and will be made available to the public after publication.

2. Program Design

The SWAS monitoring program is designed to obtain information concerning the status and trends of the acid-base chemistry of SHEN watersheds with a stratification scheme, or monitoring framework, that involves extensive and intensive components to account for both spatial and temporal variation. The SWAS monitoring program accounts for spatial variation through a site-selection strategy based on lithologic classification, and temporal variation through collection of data at different frequencies (seasonal, weekly, and episodic or hourly). Sample analysis includes pH, acid neutralizing capacity, specific conductance, sulfate, nitrate, chloride, calcium ion, magnesium ion, sodium ion, potassium ion, ammonium ion, silica, organic and inorganic monomeric aluminum, and dissolved organic carbon.[1] Table 1 provides the site id, stream name, watershed area, bedrock distribution, year of initial data collection, and sampling frequency for the 15 primary study watersheds.

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[1] Analysis of aluminum fractions and dissolved organic carbon is conducted for a subset of samples.

Table 1. SWAS primary watersheds, bedrock distribution, and sampling frequency.

SITE ID	STREAM	AREA (km^2)	% OF WATERSHED AREA			START	SAMPLING FREQUENCY
			SILICEOUS	FELSIC	MAFIC		
Predominate Bedrock: Siliceous (Siliciclastic)							
PAIN	Paine Run	12.4	100.0	0.0	0.0	1992	Weekly- Episodic
WOR1	White Oak Run	5.1	100.0	0.0	0.0	1979	Weekly
DR01	Deep Run	3.1	100.0	0.0	0.0	1979	Quarterly[1]
VT36	Meadow Run	8.9	100.0	0.0	0.0	1987	Quarterly
VT53	Twomile Run	5.6	100.0	0.0	0.0	1987	Quarterly
MAD2	Madison Run	5.2	63.1	0.0	36.9	1981	Quarterly
Predominate Bedrock: Felsic (Granitic)							
STAN	Staunton River	10.5	0.0	100.0	0.0	1992	Weekly- Episodic
VT58	Brokenback Run	9.9	0.0	93.4	6.6	1987	Quarterly
VT62	Hazel River	13.2	0.0	100.0	0.0	1987	Quarterly
NFDR	North Fork of Dry Run	2.3	0.0	100.0	0.0	1986	Quarterly[2]
Predominate Bedrock: Mafic (Basaltic)							
PINE	Piney River	12.6	0.0	31.3	69.7	1992	Weekly- Episodic
VT51	Jeremys Run	22.0	31.0	0.0	69.0	1987	Quarterly
VT61	North Fork Thornton	19.1	5.2	27.0	69.0	1987	Quarterly
VT66	Rose River	23.7	0.0	9.1	90.9	1987	Quarterly
VT75	White Oak Canyon	14.1	0.0	14.1	85.9	1987	Quarterly

[1] Deep Run was sampled weekly until 6/6/2011

[2] North Fork of Dry Run was sampled weekly until 6/7/2011

3. Number and Type of Samples Collected

Table 2 lists the total number of SHEN stream water samples collected and analyzed through the SWAS program for each of the years during the period of record, 1979 through 2016. Annual totals are provided for all samples, quarterly samples, weekly samples, and episodic samples (high-flow samples collected with ISCO automatic water samplers). The totals include samples collected in regional synoptic surveys conducted in 1987, 2000, and 2010.

The total number of samples analyzed increased in the late 1980s with initiation of weekly sampling on North Fork of Dry Run and quarterly sampling of geologically representative streams throughout SHEN. The number of samples analyzed further increased in the early 1990s with initiation of additional weekly sampling and episodic sampling on three sites selected for intensive study (PAIN, PINE, and STAN). The lower number of samples analyzed in recent years compared with the early 1990s is due to less-frequent sampling during high-discharge conditions. The number of both quarterly and weekly grab samples has been generally constant since the early 1990s. In July of 2011, however, weekly sampling on North Fork of Dry Run (NFDR) and Deep Run (DR01) was discontinued (sampling continued on a quarterly basis at these two sites). The somewhat higher number of total samples analyzed in 2010 reflects additional sampling conducted during the VTSSS 2010 survey. The relatively low number of samples analyzed in 2012 reflects low discharge and the resulting low number of episodic, high-flow samples collected that year.

The ISCO samplers are flow-level actuated. Settings for the ISCO samplers have varied during the period of record, 1992–present. In 2016, samples were collected when the flow level was above the 95th flow percentile with samples being taken every two hours. Samples were chosen for analysis with a 0.2 probability. About 20% of all samples collected were analyzed.

4. Sample Analysis Results

Complete analysis results for SWAS program samples collected in SHEN are posted on the University of Virginia Collab site, SWAS-VTSSS Agency Access, for access by the National Park Service and other supporting and collaborating natural resource management agencies as well as within NPSTORET.

Table 2 - Number of Samples Collected and Analyzed in SHEN

Year	Total Samples	Quarterly Samples	Weekly Samples	Episodic Samples
1979	15	0	15	0
1980	86	0	86	0
1981	108	0	108	0
1982	120	0	120	0
1983	107	0	107	0
1984	158	0	158	0
1985	116	0	116	0
1986	241	0	241	0
1987	420	9	350	0
1988	388	39	346	0
1989	419	40	379	0
1990	452	42	410	0
1991	456	44	412	0
1992	664	42	471	140
1993	913	36	531	336
1994	809	37	448	320
1995	560	34	386	140
1996	452	35	306	111
1997	492	36	315	140
1998	450	36	296	117
1999	434	36	300	98
2000	489	36	312	85
2001	390	36	278	76
2002	381	36	286	57
2003	751	36	316	399
2004	538	36	311	180
2005	519	36	306	177
2006	581	36	308	237
2007	361	36	289	36
2008	390	36	298	56
2009	420	36	284	100
2010	421	35	278	56
2011	406	39	247	120
2012	276	43	201	32
2013	414	44	202	165
2014	381	44	197	140
2015	398	43	194	161
2016	478	44	199	204

SWAS-VTSSS Agency Access site also includes stream water quality data collected through the VTSSS program in the western Virginia mountain region. Additional information provided on the SWAS-VTSSS Agency Access site includes sampling and analysis methods, other metadata, site documentation, and data quality assurance reports. Discharge data for sites in SHEN are also provided. Appendix 1 provides a detailed description of data and information provided on the SWAS-VTSSS Agency Access site. All data is also provided by request.

5. Comparison of 2016 Sample Analysis Results With Previous Years

Context for water quality data obtained in 2016 is provided by comparison with data obtained in previous years. Tables 3–5 compare the 2016 means for key acid-base constituents with the means for previous years' data. Separate comparisons are made for quarterly, weekly, and episodic sample sets. The ordering of sites in the presentation of these data is by watershed lithologic class.

The differences in mean values evident in Tables 3–5 between 2016 and pre-2016 samples are generally indicative of long-term change associated with acidic deposition. It should be noted, the differences between 2016 and previous years are generally small, with the exception of nitrate. Due to the gypsy moth infestation in the early 1990's, nitrate levels increased dramatically, resulting in an elevated long-term average concentration, relative to present year (2016) concentrations. More comprehensive analysis of temporal changes in stream water chemistry will be addressed in the context of periodic trend analysis.

Comparison of ANC means for quarterly samples indicates that 2 of the 15 study streams were slightly more acidic in 2016 than during the prior data collection period (PAIN and VT36). Based on weekly and episodic samples, none of the intensively monitored study streams are more acidic. ANC is an integrator of the factors that contribute to the acid-base status of surface waters, and increasing ANC is consistent with recovery from acidification in both stream water and watershed soils. The variability between quarterly and weekly sampling trends for 2016 at PAIN (quarterly data implies more acidic, weekly data implies less acidic) based on ANC is not surprising considering the small amount of variability in concentrations from one year to the next; the utility of the data set is found in the long term trend analysis.

Table 3 - Mean Values for Key Acid-Base Constituents in SHEN Study Streams: Quarterly Samples[1]

Primary Lithology	Site_ID	ANC_2016	ANC_PRE	pH_2016	pH_PRE	SO4_2016	SO4_PRE	NO3_2016	NO3_PRE	SBC_2016	SBC_PRE
Siliciclastic	DR01	10.56	8.82	5.56	5.42	89.05	98.40	0.24	2.06	129.33	133.00
Siliciclastic	PAIN	13.10	13.14	5.86	5.79	100.05	110.37	0.26	4.09	138.29	149.75
Siliciclastic	VT36	3.28	4.62	5.44	5.39	77.25	85.27	1.17	2.82	105.43	112.33
Siliciclastic	VT53	23.13	21.97	6.00	5.94	84.66	94.52	0.20	2.94	136.46	143.29
Siliciclastic	WOR1	41.22	40.11	6.26	6.08	74.49	78.95	1.56	9.04	139.43	154.25
Siliciclastic	MAD2	132.62	127.36	6.76	6.57	61.73	68.93	0.08	1.94	219.51	230.80
Granitic	NFDR	79.90	70.76	6.58	6.43	82.20	96.27	5.15	20.05	199.59	223.74
Granitic	STAN	98.83	93.19	6.90	6.58	43.84	43.05	0.10	1.38	171.35	167.37
Granitic	VT58	109.27	97.46	6.78	6.59	34.36	40.74	0.19	2.14	167.33	170.49
Granitic	VT62	120.56	106.23	6.82	6.63	29.87	36.97	0.21	2.41	182.02	181.55
Basaltic	PINE	272.55	244.51	7.19	7.01	48.09	60.77	2.93	8.10	355.33	350.97
Basaltic	VT51	262.86	233.42	7.08	6.96	91.14	111.01	0.27	5.14	390.83	387.53
Basaltic	VT61	351.21	305.97	7.24	6.96	66.23	77.92	2.38	8.63	456.38	433.70
Basaltic	VT66	189.06	164.89	6.98	6.78	42.55	50.19	5.84	11.11	268.29	267.48
Basaltic	VT75	167.44	151.40	6.92	6.73	42.26	49.89	3.85	10.18	252.10	253.15

1 Mean values are given for samples collected in 2016 and samples collected in the period, 1988–2015 (represented by _PRE). Concentration units are µeq/L and pH units.

Table 4 - Mean Values for Key Acid-Base Constituents in SHEN Study Streams: Weekly Samples[1]

Lithology	Site_ID	ANC_2016	ANC_PRE	pH_2016	pH_PRE	SO4_2016	SO4_PRE	NO3_2016	NO3_PRE	SBC_2016	SBC_PRE
Siliciclastic	PAIN	12.66	12.61	5.83	5.78	98.52	109.42	0.19	4.23	135.94	149.53
Siliciclastic	WOR1	36.75	35.32	6.20	6.06	74.84	79.31	2.07	9.27	135.73	149.41
Granitic	STAN	97.64	91.59	6.85	6.63	44.52	43.98	0.29	1.16	169.99	167.02
Basaltic	PINE	265.52	244.68	7.16	7.00	51.26	61.49	2.81	8.63	350.79	351.10

[1] Mean values are given for samples collected in 2016 and samples collected in the period, 1988–2015 (represented by _PRE). Weekly sampling began in 1992 for PAIN, STAN, and PINE. Concentration units are µeq/L and pH units.

Table 5 - Mean Values for Key Acid-Base Constituents in SHEN Study Streams: Episodic Samples[1]

Primary Lithology	Site_ID	ANC_2016	ANC_PRE	pH_2016	pH_PRE	SO4_2016	SO4_PRE	NO3_2016	NO3_PRE	SBC_2016	SBC_PRE
Siliciclastic	PAIN	12.63	8.11	5.81	5.50	93.58	110.45	3.57	10.30	133.91	157.22
Granitic	STAN	84.92	80.25	6.44	6.44	39.88	50.77	3.55	5.49	162.62	170.98
Basaltic	PINE	224.38	197.50	7.20	6.93	56.31	75.65	9.59	16.67	324.97	333.32

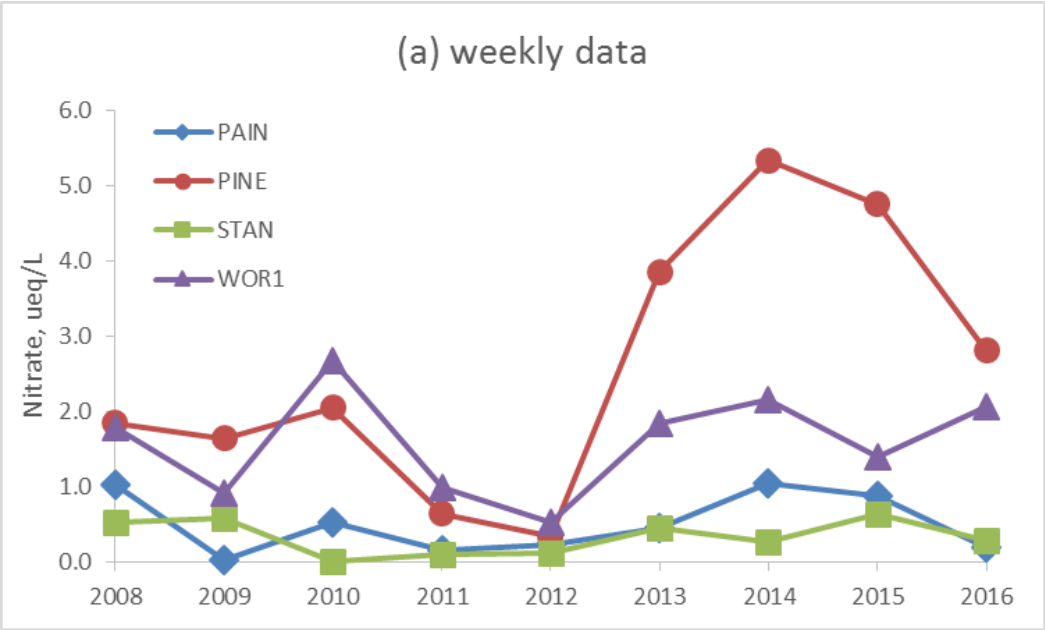
[1] Mean values are given for samples collected in 2016 and samples collected in the period, 1992–2015 (represented by _PRE). Concentration units are µeq/L and pH units.

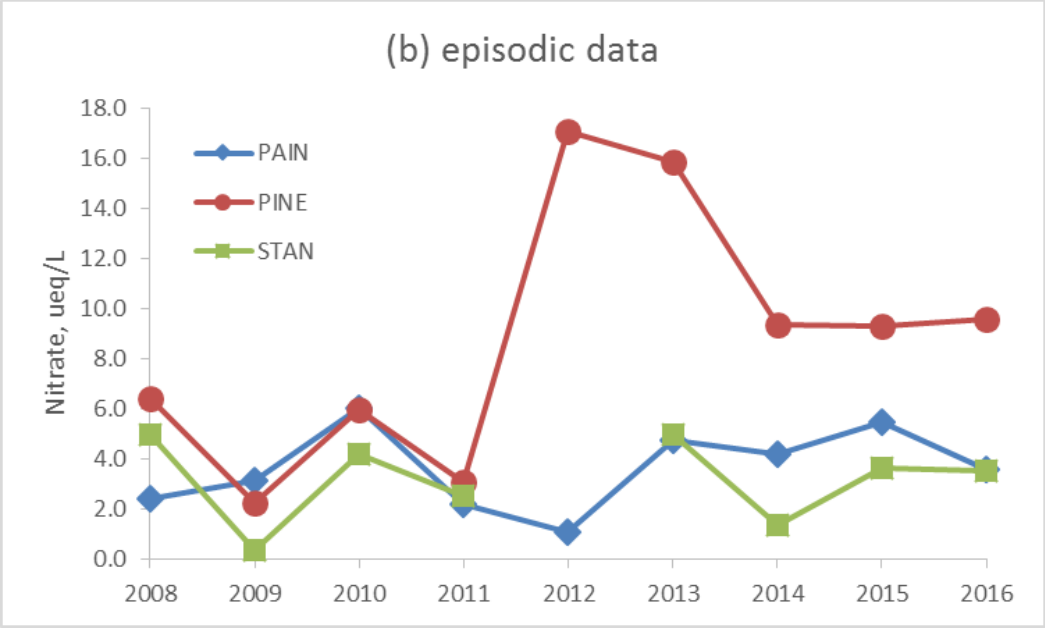
Comparison of mean pH values for 2016 with the means for previous years for quarterly, weekly and episodic sampling indicates all sites have equal or higher (less acidic) values.

Comparison of the mean sum of base cation (SBC) concentration for 2016 with the means for previous years for quarterly data indicates that 2016 means were lower than in previous years at all siliciclastic sites, two of the four granitic sites, and one of five basaltic sites. The base cations, including calcium, magnesium, sodium and potassium ion, are mainly derived from watershed soils, and depletion of base cations in watershed soils is a primary aspect of ecosystem harm associated with both acidic deposition and forest disturbance.

Comparison of mean sulfate concentrations for 2016 with the means for previous years of quarterly sampling indicates all but one site (STAN) had lower values. Comparison of mean nitrate concentrations for 2016 with the means for previous years indicates 2016 means were lower than in previous years for all sites. This is consistent with the previously observed decrease in nitrate concentrations following the transient increase associated with the gypsy moth infestation and forest defoliation in the early 1990s. In order to evaluate if current nitrate levels are changing with respect to more recent concentrations (i.e. remove bias from 1990's-2000's gypsy moth defoliation impact) a year by year comparison of mean nitrate has also been provided. Mean annual nitrate concentrations for weekly and episodic data at each of the primary sites is illustrated in Figure 2a and 2b, respectively. While between-year variability is present at all sites (+/- 1 ueq/L for weekly data and +/- 2 ueq/L for episodic data) there is a clear increase in mean nitrate concentration at PINE starting in 2013 for weekly (~ 4-5 ueq/L increase) and quarterly data (not shown) and in 2012 for episodic data (~ 6-12 ueq/L increase). For the past two (for weekly data) and three years (for episodic data), nitrate levels have been decreasing and appear to be returning to more 'typical' forest conditions. Typically, nitrate is tightly cycled in SHEN watersheds (i.e. any nitrogen inputs from the atmosphere are taken up by vegetation and very little nitrate is exported via the stream). However, if there is a disturbance to the vegetation and less or no nitrate is taken up, it may 'leak' out to the stream. This has been documented in several systems, including those in SHEN, due to insect infestations, ice damage and deforestation (Riscassi and Scanlon, 2009). The reasons for the recent nitrate increase (2012-2014) and subsequent decrease (2015-2016) at PINE is currently unknown.

Figure 2. Mean annual nitrate concentrations for SHEN watersheds sampled weekly (a) and during high flow episodes (b).





6. Examination of ANC during all flow conditions

The most extreme conditions, with respect to effects of acid-base chemistry on aquatic biota, occur during episodic high-flow conditions. High-frequency automated sampling at the sites on PAIN, PINE and STAN is designed to collect information on episodic chemistry that is missed by less-intensive grab sampling at weekly or quarterly intervals. Automatic water samplers at the three sampling sites are set to sample at two-hour intervals when discharge levels equal or exceed the 95th flow-percentile value for the season. Different actuator levels are set for higher baseflow (winter/spring) and lower baseflow (summer/fall) seasons in order to capture events throughout the year.

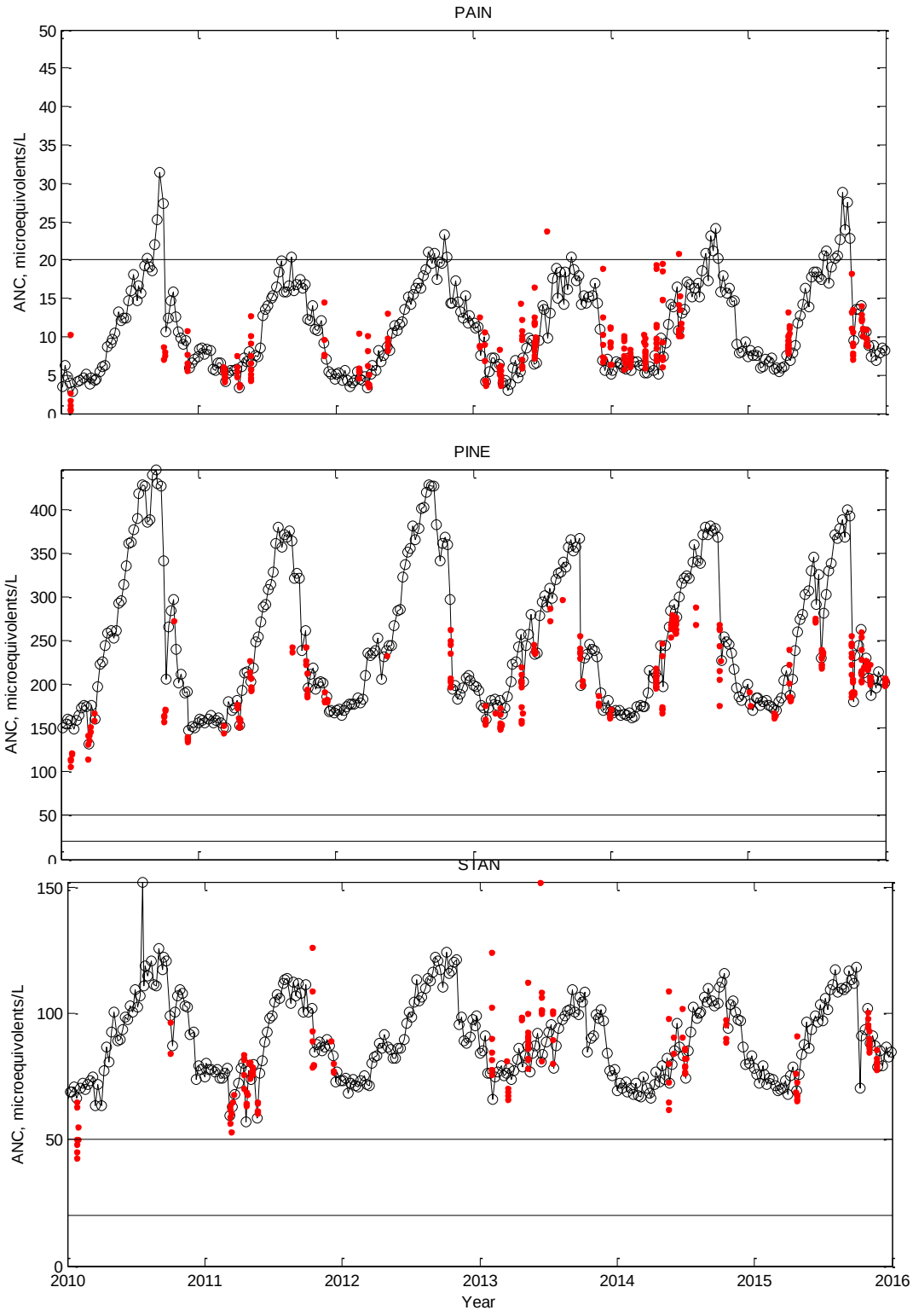
A classification scheme was determined to evaluate the response of fish to changes in acid-base status based on stream ANC and is presented in Table 6. The previous six years of ANC values for weekly grab samples and automated high-flow samples for PAIN, PINE and STAN are presented in Figure 3 along with the Brook Trout response thresholds.

Table 6 - Brook trout stream categories, ANC classes and ANC thresholds for brook trout responses (Bulger et al., 1999)

Brook trout stream category	ANC class	ANC range ($\mu equiv \cdot L^{-1}$)	Brook trout response
Suitable	Not acidic	>50	Reproducing brook trout populations expected where habitat suitable
Indeterminate	Indeterminate	20–50	Extremely sensitive to acidification; brook trout response variable
Marginal	Episodically acidic	0–20	Sublethal and (or) lethal effects on brook trout possible
Unsuitable	Chronically acidic	<0	Lethal effects on brook trout probable

For all three streams, lower ANC levels occur late fall through early spring, which is the part of the year (October through March) when sensitive life stages (eggs and fry) of the brook trout (*Salvelinus fontinalis*) are present in SHEN streams. The most-extreme or critically low ANC depressions occur in PAIN. Episodically depressed ANC values are also observed on STAN and PINE, but have not dropped below 50 µeq/L since 2010 (STAN).

Figure 3. ANC values for grab (open circles) and automated episodic (closed dots) samples in 2010-2016. The brook trout response to the 20 and 50 microequivalent threshold marked in the graphs are described in Table 6.



7. Discharge

Discharge gauges were maintained at four SWAS study sites through the end of 2016. Note, gauging on NFDR was discontinued in September of 2011. Figure 4 displays inter-annual variation in the individual annual mean discharge (units of cfs) around the long-term (1993 through 2016) mean discharge (units of cfs) for each of the five gauging sites in SHEN. For PAIN, PINE, and WOR1, the mean annual discharge rate was higher in 2016 as compared to the long-term annual mean, ranging between 15% at WOR1 to 30% higher at PINE. The 2016 mean discharge at STAN was 29% lower than the long-term annual mean.

Table 7. Annual minimum daily discharge (cfs) in SHEN study streams from 1993-2016

	NFDR	PAIN	PINE	STAN	WOR1
1993	0.12	0.11	0.28	1.05	0.00
1994	0.64	0.15	0.76	2.25	0.00
1995	0.06	0.50	1.22	3.45	0.02
1996	0.23	0.73	2.02	1.33	0.01
1997	0.01	0.05	0.17	0.64	0.00
1998	0.01	0.03	0.09	0.54	0.00
1999	0.01	0.00	0.04	0.15	0.00
2000	0.03	0.24	0.34	0.61	0.00
2001	0.05	0.04	0.36	1.17	0.00
2002	0.01	0.05	0.12	0.87	0.00
2003	0.05	0.93	0.56	2.67	0.07
2004	0.00	0.80	0.61	0.97	0.01
2005	0.05	0.11	0.44	1.43	0.00
2006	0.10	0.08	0.67	1.48	0.00
2007	0.03	0.08	0.62	0.02	0.00
2008	0.07	0.06	0.69	0.00	0.00
2009	0.03	0.14	0.57	0.29	0.00
2010	0.04	0.00	0.47	0.48	0.00
2011	0.14	0.47	0.21	1.63	0.00
2012	-	0.48	0.35	0.31	0.00
2013	-	0.71	0.78	0.96	0.03
2014	-	0.58	0.71	3.49	0.00
2015	-	0.58	1.04	3.04	0.00
2016	-	1.48	2.34	3.18	0.06

Table 8. Annual maximum daily discharge (cfs) in SHEN study streams from 1993-2016

	NFDR	PAIN	PINE	STAN	WOR1
1993	27.73	212.71	91.54	46.32	64.63
1994	10.87	58.52	66.99	33.02	61.80
1995	23.44	246.24	111.28	69.38	132.84
1996	71.46	551.23	309.69	305.96	183.17
1997	82.78	123.43	115.46	39.59	34.39
1998	134.35	211.89	161.10	128.47	44.27
1999	42.69	87.81	290.53	359.87	24.31
2000	9.17	72.90	43.90	34.16	9.02
2001	29.30	56.42	59.08	25.67	55.74
2002	6.15	65.42	52.22	266.68	26.09
2003	169.83	508.09	663.02	284.26	219.30
2004	53.12	382.39	376.71	143.30	111.56
2005	190.88	510.71	332.36	298.74	90.24
2006	44.99	108.88	664.68	43.87	43.68
2007	4.09	47.51	32.56	23.89	17.94
2008	20.72	41.67	82.77	62.70	16.44
2009	24.91	96.02	108.40	55.38	49.05
2010	201.48	399.82	578.89	546.46	148.72
2011	75.79	402.07	736.21	286.51	93.79
2012	-	300.23	99.86	19.05	36.25
2013	-	287.91	525.98	270.52	76.62
2014	-	307.58	577.52	48.18	105.03
2015	-	177.69	315.65	29.80	65.83
2016	-	94.73	171.17	18.53	32.50

Figure 4. Inter-annual variation in discharge around the long-term mean (1993 through 2016) discharge for gauged streams in SHEN. NFDR gauge was discontinued in 2011.

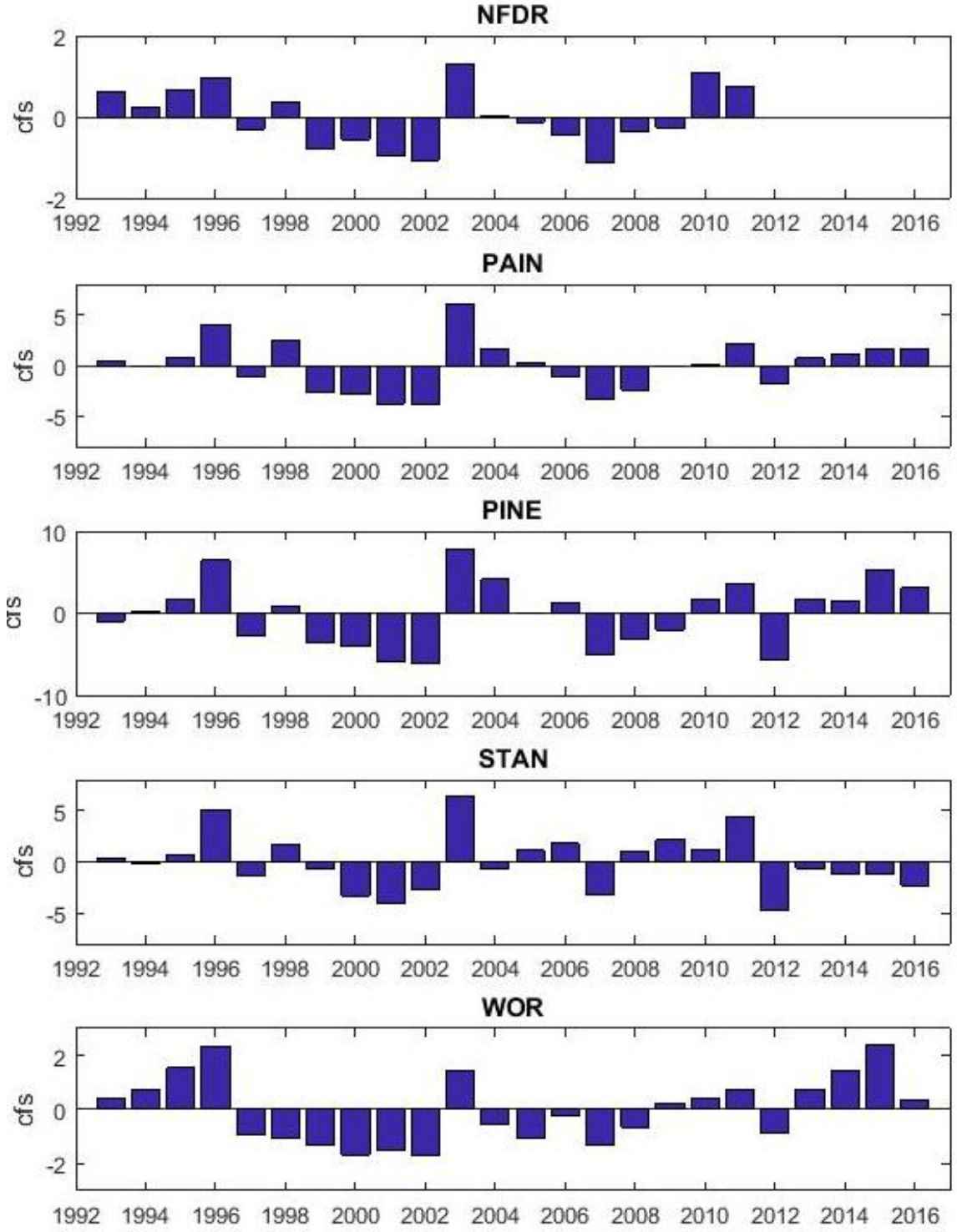


Figure 5. Box-whisker plots of mean daily discharge for the period of record (1993-2016). On each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the '+' symbol. Circles represent the maximum, mean, and minimum daily discharge for each month of 2016.

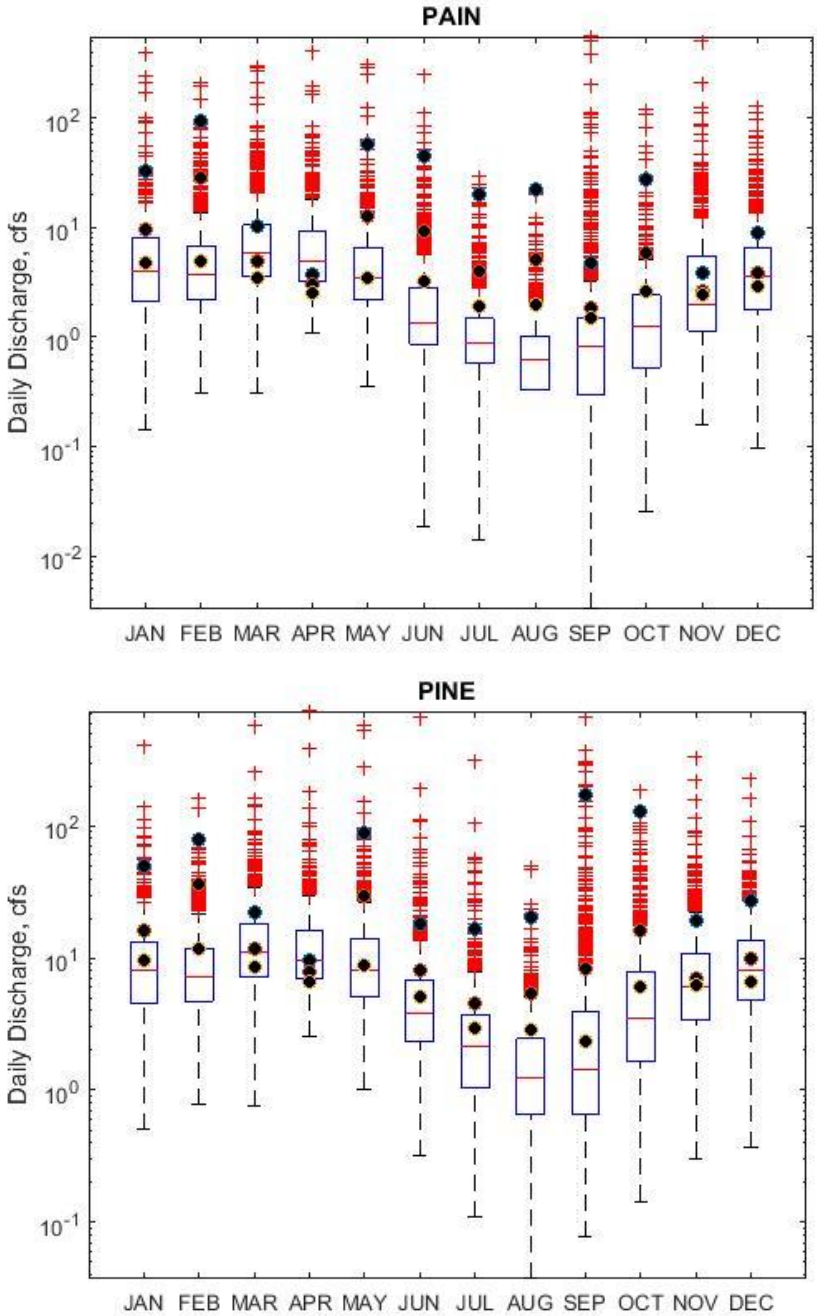
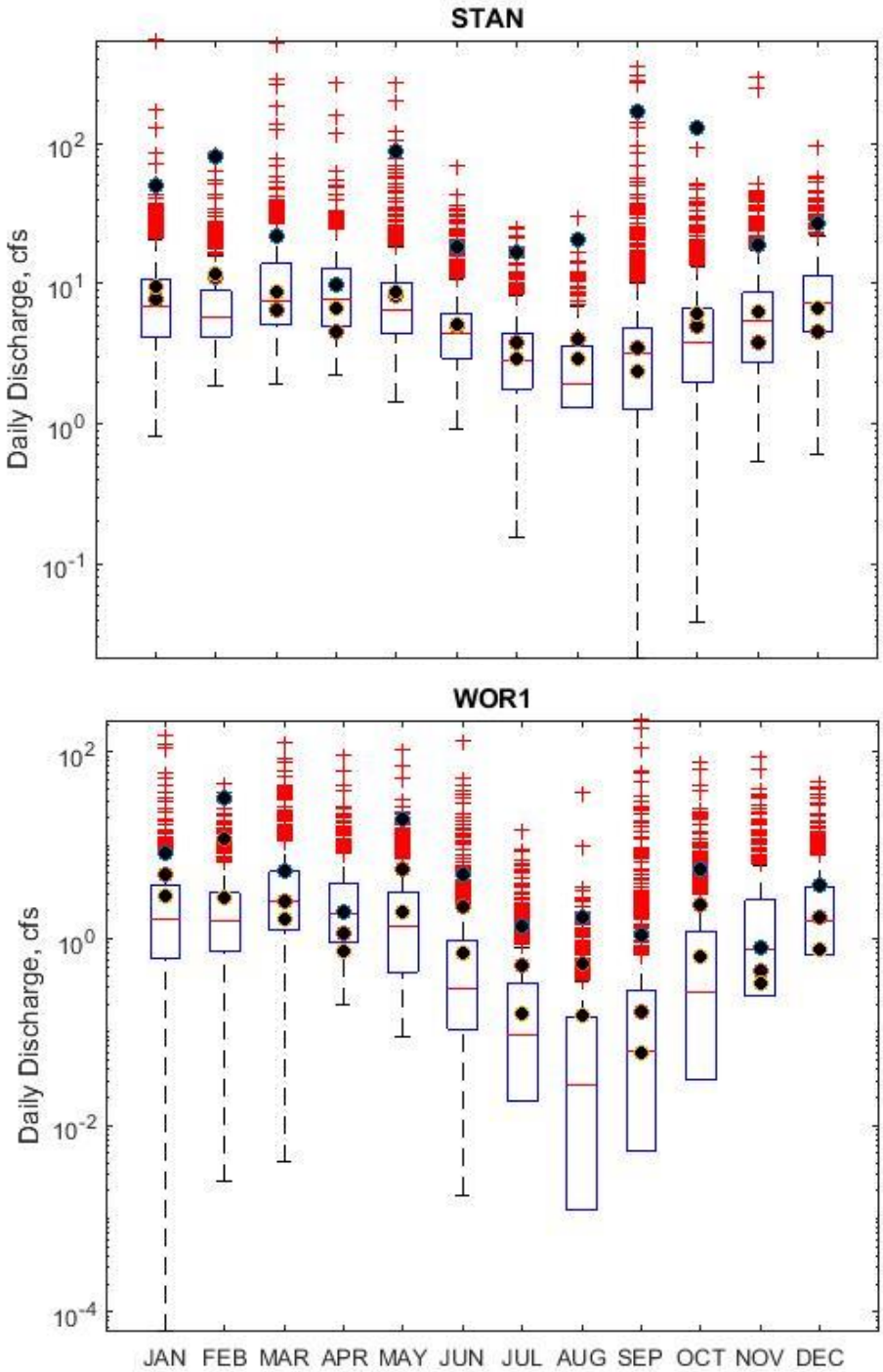


Figure 5. Box-whisker plots of mean daily discharge for the period of record (1993-2016). On each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the '+' symbol. Circles represent the maximum, mean, and minimum daily discharge for each month of 2016.



7. Water Temperature

Stream temperature has been measured at weekly site visits at all sites since 1993. The maximum temperature measured for each site ranged from 21.0 to 21.5 ºC (Table 9) and occurred in either July or August (Figure 6).

Table 9. Annual maximum weekly water temperature (ºC) in SHEN study streams from 1993-2016.

	PAIN	PINE	STAN	WOR1
1993	23.00	20.00	21.00	22.00
1994	23.00	19.00	18.50	23.00
1995	21.00	22.00	22.00	22.00
1996	20.00	21.00	22.00	21.00
1997	22.50	19.00	22.00	20.00
1998	22.00	20.00	22.00	24.00
1999	24.00	19.00	25.00	22.00
2000	21.00	18.00	21.00	22.00
2001	21.00	19.00	22.00	22.50
2002	23.00	20.00	24.00	24.00
2003	21.30	18.50	21.00	21.00
2004	21.40	20.00	21.00	20.00
2005	24.00	21.00	20.50	21.00
2006	23.00	22.00	23.00	21.50
2007	25.00	22.00	23.00	23.00
2008	24.00	21.00	20.50	23.00
2009	22.40	20.40	20.00	20.50
2010	26.50	23.00	23.00	25.00
2011	22.50	23.00	21.70	20.80
2012	23.50	21.00	21.50	24.00
2013	20.70	19.40	18.80	20.20
2014	20.20	19.00	18.40	19.70
2015	21.80	21.90	19.50	21.00
2016	21.10	21.50	21.00	21.40

Table 10. Annual minimum weekly water temperature (ºC) in SHEN study streams from 1993-2016.

	PAIN	PINE	STAN	WOR1
1993	1.50	2.00	2.50	2.00
1994	2.00	1.00	0.50	3.00
1995	0.00	0.50	0.00	1.50
1996	1.00	2.00	2.00	2.50
1997	0.00	0.50	1.00	3.00
1998	3.00	4.00	5.00	2.00
1999	1.00	1.00	1.00	3.50
2000	0.00	0.00	1.00	2.00
2001	0.00	0.00	1.00	1.00
2002	0.00	0.50	1.50	0.00
2003	0.00	0.00	0.00	1.50
2004	0.60	0.30	0.90	2.00
2005	0.50	1.50	3.00	3.00
2006	2.50	2.80	3.50	3.50
2007	0.00	0.00	0.50	1.00
2008	1.00	0.00	0.00	1.50
2009	0.50	1.50	2.00	3.50
2010	1.50	1.50	2.50	3.00
2011	1.00	1.50	2.00	2.50
2012	3.00	2.00	2.00	3.50
2013	2.00	2.30	3.10	3.10
2014	0.40	0.30	0.90	1.80
2015	0.00	0.00	0.20	0.90
2016	1.40	0.00	1.30	1.90

Figure 6. Box-whisker plots of weekly water temperature for the concurrent POR (1993-2016). On each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the '+' symbol. Circles represent the maximum, mean, and minimum weekly water temperature for each month of 2016.

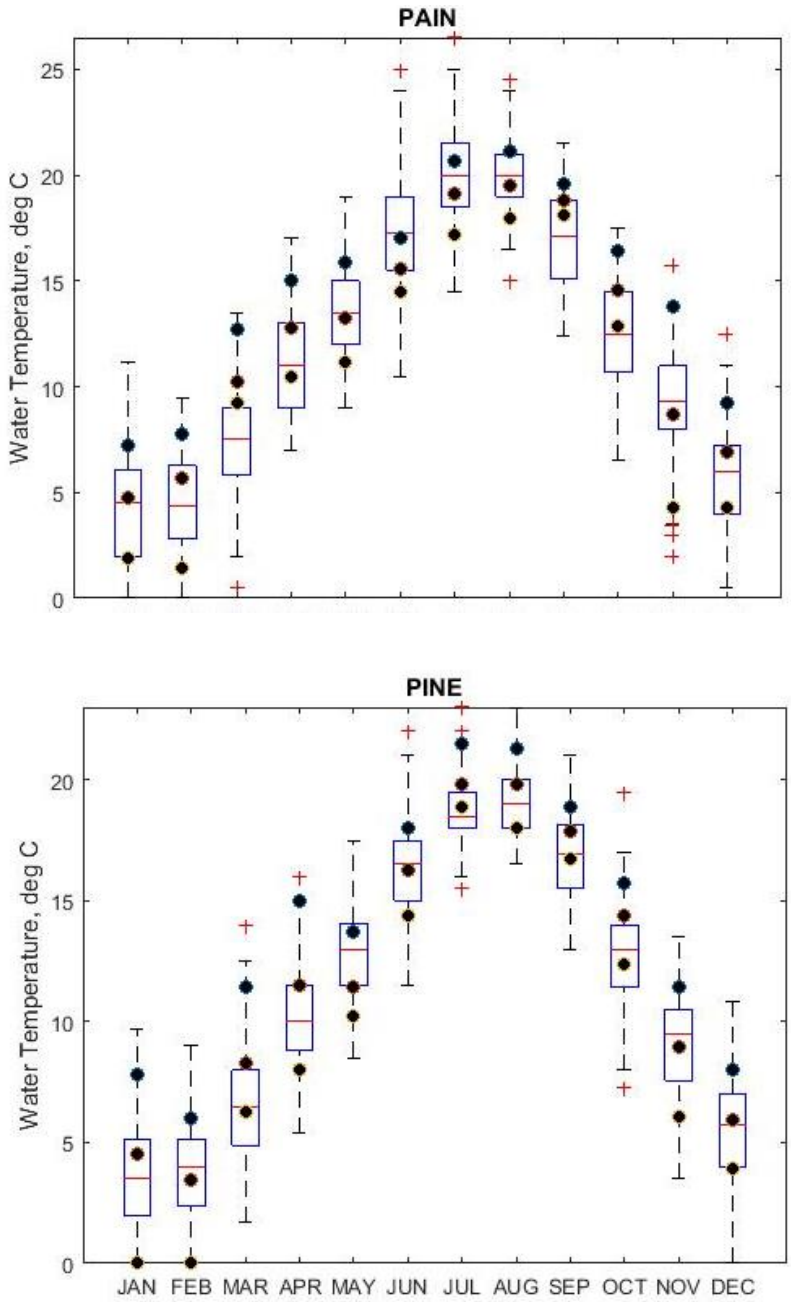
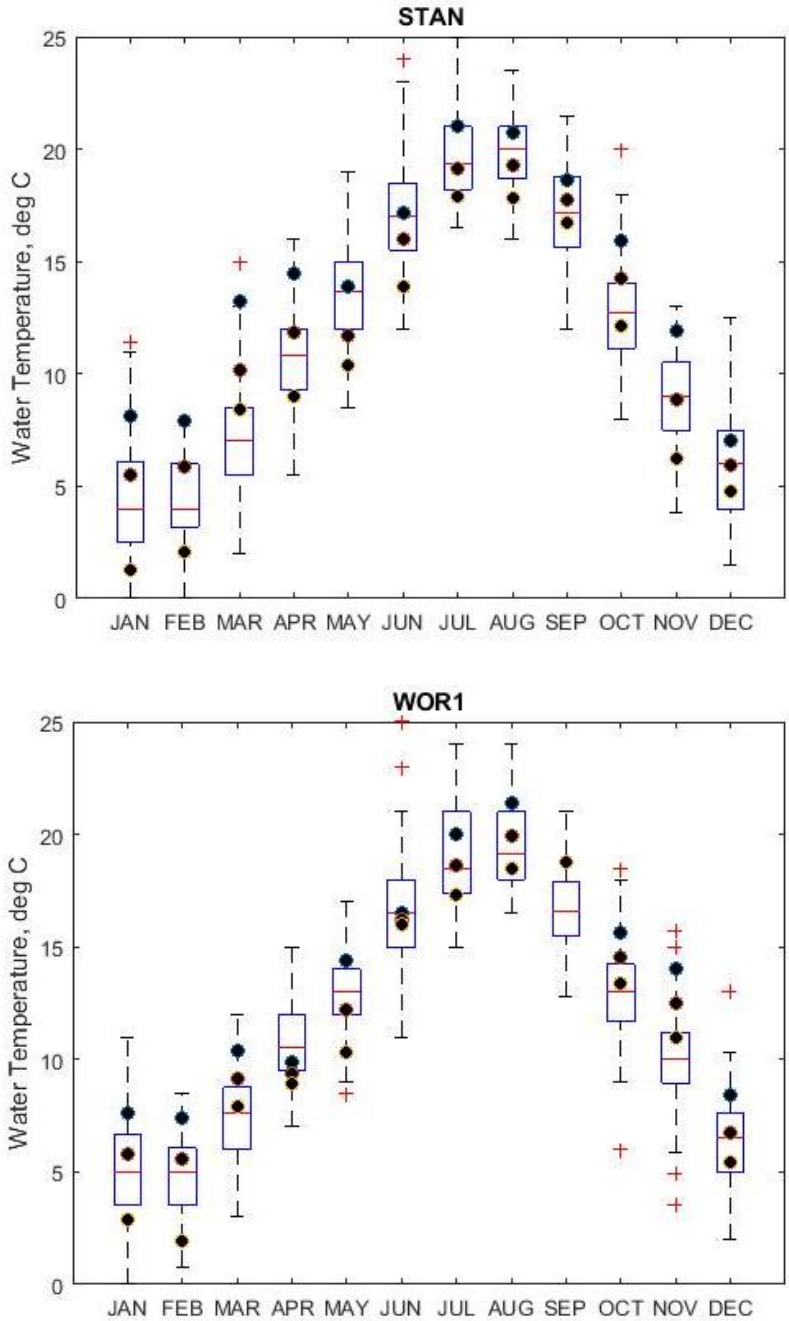


Figure 6. Box-whisker plots of weekly water temperature for the concurrent POR (1993-2016). On each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the '+' symbol. Circles represent the maximum, mean, and minimum weekly water temperature for each month of 2016



8. SWAS-VTSSS Related Publications and Presentations: 2009–2016

Jensen, A.J., Riscassi, A.L., and T.M. Scanlon, in press. The effect of wildfire on streamwater mercury and organic carbon in a forested watershed in the southeastern United States. *Environmental Science: Processes & Impacts*

Robison, A.L. and T.M Scanlon, in preparation. Climate change to offset improvement in watershed acid-base status provided by Clean Air Act and Amendments: A model application in Shenandoah National Park, Virginia. *Water Resources Research.*

Stoken, O. M., A. L. Riscassi, and T. M. Scanlon, Association of dissolved mercury with dissolved organic carbon in U.S. rivers and streams: The role of watershed soil organic carbon, *Water Resources Research*, doi:10.1002/2015WR017849, 2016.

Rice, K.C., and Jastram, J.D. 2015. Rising air and stream-water temperatures in Chesapeake Bay region, USA. *Climate Change*, 128 (1-2) pp. 127-138

Rice, K.C., Jastram, J.D., Wofford, J.E.B., and Schaberl, J.P. 2014. Synthesis of thirty years of surface-water quality and aquatic-biota data in Shenandoah National Park: Collaboration between the U.S. Geological Survey and the National Park Service: The George Wright Forum**:** vol. 31 (2), p. 198-204

Rice, K.C., Scanlon, T.M., Lynch, J.A., and Cosby, B.J. 2014. Decreased Atmospheric Sulfur Deposition across the Southeastern U.S.: When Will Watersheds Release Stored Sulfate? *Environmental Science and Technology*, 28 (17) pp. 10071-10078, doi:10.1021/es501579s

Converse, A.D., Riscassi, A.L and T.M. Scanlon. 2014. Seasonal contribution of dewfall to mercury deposition determined using a micrometeorological technique and dew chemistry, *Journal of Geophysical Research – Atmospheres, 119, p1-9.*

Robison, A.L., T.S. Scanlon, B.J. Cosby, J.R. Webb, and J.N. Galloway. 2013. Roles of sulfate

adsorption and base cation supply in controlling the chemical response of streams of western Virginia to reduced acid deposition. *Biogeochemistry,* doi:10.1007/s10533-013-9921-6.

Gunda, T., and T.M. Scanlon. 2013. Topographical influences on the spatial distribution of soil mercury at the catchment scale. *Water, Air & Soil Pollution*, 224:1511, doi: 10.1007/s11270-013-1511-7.

Riscassi, A.L., and T.M Scanlon. 2013. Factors controlling dissolved and particulate mercury export from three forested, upland Appalachian catchments. *Journal of Hydrology*, 501, 92-100, doi:10.1016/j.jhydrol.2013.07.041.

Rice, K.C. and J.R. Price, J.R. 2013. Comparison of mineral weathering and biomass nutrient uptake in two small forested watersheds underlain by quartzite bedrock, Catoctin Mountain, Maryland, USA. *Aquatic Geochemistry*: doi 10.1007/s10498-013-9205-8.

Deviney, Jr., F.A., D.E. Brown, and K.C. Rice. 2012. Evaluation of Bayesian estimation of a hidden continuous-time Markov Chain Model with application to threshold violation in water-quality indicators. *Journal of Environmental Informatics*, 19(2):70-78, doi: 10.3808/jei.201200210.

Webb, J.R. 2011. Virginia Trout Stream Sensitivity Study 2010 Survey: Results for Shenandoah National Park. Project Report, U.S. Department of the Interior, National Park Service.

Snyder, C.D., J.R. Webb, J.A. Young, Z.B. Johnson. 2011. Biological Significance of Headwater Streams and Perennial Springs in Shenandoah National Park. NRPP Final Report to U.S. Department of the Interior, National Park Service.

Riscassi, A. L., Hokanson, K .J., T. M. Scanlon. 2011. Streamwater particulate mercury and suspended sediment dynamics in a forested headwater catchment, *Water, Air, and Soil Pollution*, doi:10.1007/s11270-010-0731-3.

Riscassi, A. L., T. M. Scanlon. 2011. Controls on stream water dissolved mercury in three mid-Appalachian forested headwater catchments, *Water Resources Research*, 47, W12512, doi:10.1029/2011WR010977.

Miller, J.L. 2011. Chemical Changes in Virginia's Brook Trout Streams: An Analysis of Statewide Surveys 1987-2010. Master's Thesis, Department of Environmental Sciences, University of Virginia.

Sullivan, T.J., B.J. Cosby, T.C. McDonnell. 2010. Aquatic Critical Loads and Exceedances in Acid-Sensitive Portions of Virginia and West Virginia. Report to National Park Service, USEPA, USDA Forest Service, and USGS.

Riscassi, A. and T. M. Scanlon, (2009) Nitrate variability in hydrological flow paths for three mid-Appalachian forested watersheds following a large-scale defoliation, *Journal of Geophysical Research – Biogeosciences*, 114, G02009.

Presentations

Jensen, A.J., Riscassi, A.L., and T.M. Scanlon. 2017. The effect of wildfire on stream mercury and organic carbon in a Southern Appalachian forested watershed in the Eastern United States. International Conference on Mercury as a Global Pollutant (ICMGP) 2017. Providence, RI.

Riscassi, A.L., Camper, T., Lee, T., Druckenbrod, D. and T.M. Scanlon. 2016. Tree Rings as Chroniclers of Mercury Exposure in Shenandoah National Park, Virginia, American Geophysical Union Fall 2016, San Francisco, CA (invited speaker)

Riscassi, A.L. 2016. Thirty-seven years of monitoring Virginia's mountain streams: Understanding the relationship between the atmosphere, land, water and biota. Pesentation to the Rivanna Master Naturalists. Charlottesville, Virginia.

Camper, T. 2016. Tree Cores as Chroniclers of Mercury Exposure in the Shenandoah National Park. Undergraduate Research, Environmental Sciences Department, Univeristy of Virginia. Charlottesville, VA.

Rhea, A. 2016. Spatial Variation of Dissolved Organic Carbon and Nitrate in Paine Run, Shenandoah National Park. Undergraduate Research, Environmental Sciences Department, Univeristy of Virginia. Charlottesville, VA.

Galloway, J. N. 2016. Virginia's Mountain Streams, Sentinels of Change. Thomas Jefferson Awards. Virginia Museum of Natural History.

Atkins, J.W. and A.L. Riscassi. 2015. Impact of episodic acidification on brook trout in Shenandoah National Park. University of Virginia Huskey Research Exhibition. Charlottesville, Virginia. – [*First place poster in Biological and Biomedical Sciences 2 session*].

Jastram, J.D., and Rice, K.C. 2015. Synthesis of thirty years of surface-water quality and aquatic-biota data in Shenandoah National Park: Collaboration between the U.S. Geological Survey and the National Park Service: GSA national meeting, Nov. 1-4, 2015; Baltimore, Md.

Rice, K.C., Scanlon, T.M., Lynch, J.A., and Cosby, B.J., 2015, Decreased atmospheric sulfur deposition across the southeastern U.S.: When will watersheds release stored sulfate?: Acid Rain 2015, Oct. 19-23; Rochester, NY

Riscassi, A.L., Scanlon, T.M. and J. Cummings. 2015. Delayed and variable recovery from acid deposition in Shenandoah National Park streams: A story of geologic history, long-term monitoring, and management of air and water resources. 9th International Conference on Acid Deposition. Rochester, NY.

Scanlon, T. M., K. C. Rice, A. L. Riscassi, and B. J. Cosby. 2015. Sulfur mass balances of forested catchments: Improving predictions of stream sulfate concentrations through better representation of soil storage and release, American Geophysical Union Fall Meeting, San Francisco, CA.

Scanlon, T.M., Robison, A.L. and A.L. Riscassi. 2015. Modeling the impact of climate change on the acid-base status of a forested, upland watershed in Shenandoah National Park, Virginia. 9th International Conference on Acid Deposition. Rochester, NY.

Rice, K.C., Scanlon, T.M., Lynch, J.A., and Cosby, B.J. 2014. Decreased Atmospheric Sulfur Deposition across the Southeastern U.S.: When Will Watersheds Release Stored Sulfate? American Geophysical Union 2014 Fall Meeting, San Francisco, CA.

Riscassi, A.L., A.L. Robison, T.M. Scanlon, B.J. Cosby, J.R. Webb, and J.N. Galloway. 2014. Geologic controls on the chemical stream water response to atmospheric pollution (acid and Hg deposition) in Shenandoah National Park. Geological Society of America Annual Meeting, Vancouver, Canada.

Stoken, O. M., A. L. Riscassi, and T. M. Scanlon. 2014. Association of dissolved mercury with dissolved organic carbon in rivers and streams: The role of watershed soil organic carbon, American Geophysical Union 2014 Fall Meeting, San Francisco, CA. – [*Winner, Outstanding Student Presentation Award*].

Robison, A. L., T. M. Scanlon, B. J. Cosby, J. R. Webb, J. N. Galloway. 2013. Controls on Acid Recovery in Western Virginia Streams: Past, Present, and Future. U.S.-Japan Joint Seminar on Catchment Hydrology and Forest Biogeochemistry, Honolulu, Hawaii.

Webb, J.R. 2012. The SWAS-VTSSS Program. Appalachian Stewardship Foundation Directors Meeting, Hawks Nest State Park, WV.

Scanlon, T. M., A. L. Riscassi. 2012. Controls on mercury transport from forested headwater catchments in Shenandoah National Park and beyond. American Geophysical Union 2012 Fall Meeting, San Francisco, CA.

Robison, A. L., T. M. Scanlon, B. J. Cosby, J. R. Webb, J. N. Galloway. 2012. Base cation controlled recovery from acidification in streams in the Ridge/Blue Ridge provinces. American Geophysical Union 2012 Fall Meeting, San Francisco, CA.

Webb, R. 2011. Virginia Trout Stream Sensitivity Study: 2010 Survey. Summary presentation. Access at http://swas.evsc.virginia.edu/VTSSS-2010/Reports/VTSSS-080111.pdf

Webb, R. J. Miller, J. Cosby, J. Galloway, S. Maben. 2011. The Virginia Trout Stream Sensitivity Study 2010 Survey: Evidence for Recovery from Acidification. Southern Division American Fisheries Society East Coast Trout Workshop, Frostburg, MD.

Scanlon, T. M. 2011. Stream water nitrogen dynamics: Recent findings from the Shenandoah Watershed Study. Virginia Tech, Department of Forest Resources and Environmental Conservation. Blacksburg, VA.

Riscassi, A.L., T.M. Scanlon. 2011. Controls on streamwater HgD and DOC export from three mid-Appalachian forested headwater catchments. The 10th International Conference on Mercury as a Global Pollutant (ICMGP), Halifax, Nova Scotia.

Riscassi, A. L., Hokanson, K. J., T. M. Scanlon. 2010. Streamwater particulate mercury and suspended sediment dynamics in a forested headwater catchment. American Geophysical Union 2010 Fall Meeting, San Francisco, CA.

APPENDIX 1

UVA Collab Site: SWAS-VTSSS DATA WAREHOUSE

Contents Description

- Data associated with SWAS-VTSSS primary data collection sites, including sites in George Washington and Jefferson National Forests, Shenandoah National Park, and Virginia Wildlife Management Areas, and on other public and private lands.

- Data associated with TIME project data collection sites, including sites in Virginia, West Virginia, and Maryland.

- File names include the date of the most-recent update in YYYYMMDD format.

(1) CHEMISTRY DATA

Data are provided in Access and Excel formats.

A. ACCESS TABLES

SWAS_VTSSS_PRIMARY_YYYYMMDD.accdb **-** Access database with sample analyses and related data tables.

DATA_MODEL_YYYYMMDD.jpg - Diagram of table relationships for SWAS_VTSSS_PRIMARY_YYYYMMDD.accdb; shows table alignment but not table linkage (referential integrity is not enforced).

Tables included in SWAS_VTSSS_PRIMARY_YYYYMMDD.accdb:

SAMPLE_MEASUREMENTS_YYYYMMDD - Sample analysis results in row-major format, with separate row for each analysis result.

Data table creation, rules and notes

- includes records for samples with complete analysis, defined as including pH, ANC, SO4, NO3, Cl, Ca, Mg, K, Na
- includes additional analysis, if available, for samples with complete analysis
- values below method detection limits (MDLs) have not been censored (applies to some NO3, NH4, DOC, TMAL, and OMAL values)
- the Sample field is unique for each sample
- Synoptic, Quarterly, Weekly, and Episodic fields indicate association of sample records with specific data sets
- sample records may be associated with multiple data sets

SAMPLE_COLLECTOR_OBSERVATIONS_YYYYMMDD - Qualitative observations associated with sample collection, including weather, stream flow level, and stream turbidity.

SWAS_VTSSS_PRIMARY_SITE_DOCUMENTATION_YYYYMMDD - Site documentation data for primary SWAS-VTSSS sites, including current and historic synoptic survey, quarterly, weekly, and episodic sample sites, including date ranges for sample collection associated with specific data sets, stream and watershed disturbance notes, and site or map discrepancy notes.

LOCAL_CHARACTERISTICS_YYYYMMDD - Associates sample records with specific suites of sample collection, handling, preparation, and analysis methods.

METHODS_SAMPLE_COLLECTION_YYYYMMDD - Field method: grab sample or automated sample collection**.**

METHODS_SAMPLE_HANDLING_YYYYMMDD - Sample container, storage, and transport.

METHODS_SAMPLE_PREPARATION_YYYYMMDD - Sample treatment and preservation.

METHODS_SAMPLE_ANALYSIS_YYYYMMDD - Sample analysis technique, equipment, citations.

METHODS_MDL_YYYYMMDD - Methods for determination of method detection limits and citations.

B. EXCEL SPREADSHEETS

SWAS_VTSSS_ PRIMARY_YYYYMMDD.xlsx - Spreadsheet with sample analyses in column-major format: analysis results are included in single rows for each sample. Explanatory text (derivation, rules for data set creation, notes) are provided at the top of the spreadsheet.

C. DATA QUALITY REPORTS

Prior to 2009, before SWAS-VTSSS data were posted on UVA Collab, data quality reports were combined with data reports. ZIP files are provided for reports that include multiple files.

(2) DISCHARGE DATA

SWAS_Discharge_YYYYMMDD.zip - Tables with daily and hourly discharge estimates (CFS) for streams in Shenandoah National Park, including White Oak Run, North Fork of Dry Run, Paine Run, Staunton River, and Piney River.

(3) SITE DOCUMENTATION

A. EXCEL SPREADSHEETS

SWAS_VTSSS_PRIMARY_SITE_DOCUMENTATION_YYYYMMDD.xlsx - Site documentation data for primary SWAS-VTSSS sites, including current and historic synoptic survey, quarterly, weekly and episodic sample sites, including date ranges for sample collection, stream and watershed disturbance notes, and site or map discrepancy notes. Explanatory text provided at the top of the spreadsheet. This an Excel version of the SWAS_VTSSS_PRIMARY_SITE_DOCUMENTATION_YYYYMMDD table included in the Access database, SWAS_VTSSS_PRIMARY_YYYMMDD.accdb.

B. PDF FILES

Station reports in PDF formats, including site descriptions, coordinates, elevation, access descriptions, photographs, and maps.

(a) SWAS-VTSSS_PRIMARY_SITES

Station reports for SWAS-VTSSS primary sites in western Virginia provided as zip files for individual counties.

(b) TIME SITES

Station reports for TIME project sites in Virginia, West Virginia, and Maryland provided as a single zip file.