

Smoky Mountains Water Quality Annual Report for 2002

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April 11, 2003

**Report Prepared For:
The National Park Service
Cooperative Agreement No.: 1443-CA-5460-98-006**

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TABLE OF CONTENTS

	Page
1. Noland Divide Watershed	1
1.1 Annual Deposition Rates	1
1.2 Soil Lysimeter Chemistry	5
1.3 Weather Station Summaries	6
2. Stream Survey Results	12
3. Overall QA/QC Procedures	20
3.1 Ion Chromatography QA/QC Procedures	20
3.2 Atomic Absorption QA/QC Procedures	24
3.3 Ion Balance	27
3.4 Inter-laboratory Comparison Results	27
3.5 Data Completeness	28
Appendix A-1: Executive Summary of Report Entitled: Aluminum Analysis Assessment Report	
Appendix A-2: Executive Summary of Report Entitled: Water Quality and BMP Monitoring Report for Tunnel Reconstruction in the Great Smoky Mountains National Park	

List of Tables

Table 1-1. Statistical summeries for pH and conductivity from the soil lysimeters	5
Table 1-2. Statistical summeries of the anion chemistry analysis on the soil lysimeter samples	5
Table 1-3. Statistical summeries of the cation chemistry analysis on the soil lysimeter samples	6
Table 1-4. Statistical summary air temperature for Noland Divide Watershed	7
Table 2-1. Median water quality values	14
Table 2-2. Percentage change in 2002 median water quality values from 1993-2002 data	16
Table 2-3. Descriptive statistics of 2002 median water quality values	18
Table 2-4. pH effects and number of sampling sites by pH range	19
Table 3-1. Analytical procedures for chemistry analysis preformed at the University of Tennessee	20
Table 3-2. QA\QC results of the IC analysis for selected anions	21
Table 3-3. QA\QC results of the IC analysis for monovalent cations	21
Table 3-4. Average QA\QC results of the AA analysis for magnesium and calcium	24
Table 3-5. Average ion balances for both streamlets, precipitation and throughfall	27
Table 3-6. Individual scores or each analyte submitted to the USGS analytical evaluation program. All concentration data given in ppm, and conductivity given in $\mu\text{S}/\text{cm}$.	28
Table 3-7. Wet-only and throughfall measurements and estimates for annual precipitation amounts entering the NDW in 2001	29

List of Figures

Figure 1-1. Total Inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation	2
Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation	3
Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW	4
Figure 1-4. Daily average air temperature measured at the Noland Divide Watershed	7
Figure 1-5. Percent wind direction for Noland Divide Watershed	8
Figure 1-6. Relative humidity for the Noland Divide Watershed	9
Figure 1-7. Soil water content for Noland Divide Watershed	10
Figure 1-8. Soil temperature for Noland Divide Watershed	11
Figure 2-1 Median pH Values by elevation	18
Figure 3-1. Sulfate concentrations made on laboratory check sample over multiple runs	22
Figure 3-2. Potassium concentrations made on laboratory check sample over multiple runs	23
Figure 3-3. Magnesium standard check sample results plotted over the course of the analysis	25
Figure 3-4. Calcium standard check sample results plotted over the course of the analysis	26

This report describes calendar year (CY) 2002 work accomplished under Amendment No. 6 to Cooperative Agreement No. **1443-CA-5460-98-006** between the National Park Service and the University of Tennessee for 'Water Quality Monitoring in the Great Smoky Mountains National Park.'

1.0 Noland Divide Watershed

1.1 Annual Deposition Rates

During the year 2002, the amount of total inorganic nitrogen entering the Noland Divide Watershed (NDW) as throughfall was 1113 equivalents of nitrogen per hectare per year (eq/ha/yr), and 494 (eq/ha/yr) was collected as wet-only precipitation (see Figure 1-1). These deposition rates were very close to the 10 year average deposition rates recorded since the project began in 1991.

The amount of sulfate entering the NDW as throughfall was 1542 (eq/ha/yr), and 480 (eq/ha/yr) as wet-only precipitation (Figure 1-2). These deposition rates were below the 10 year average deposition rates for sulfate. The difference between precipitation inputs and throughfall inputs represents a very good estimate of the dry and cloudwater inputs to these systems (Shubzda *et al.*, 1995). Unlike nitrogen, sulfate flux represents a very good estimate of the total deposition rate entering a watershed, because foliar uptake and/or leaching is minimal (Garten *et al.*, 1988; Lindberg and Garten, 1988).

The annual rainfall amount collected during 2002 was 216 cm, while surrounding lowland areas such as Knoxville, TN generally average around 109 cm/yr (Figure 1-3). This difference in precipitation volume can be attributed to orographic effects. Orographic precipitation occurs as moist air is forced over mountains, the vapor pressure decreases, and the moist air reaches a saturation point, where increased precipitation occurs (Barry and Schemenauer, 1986).

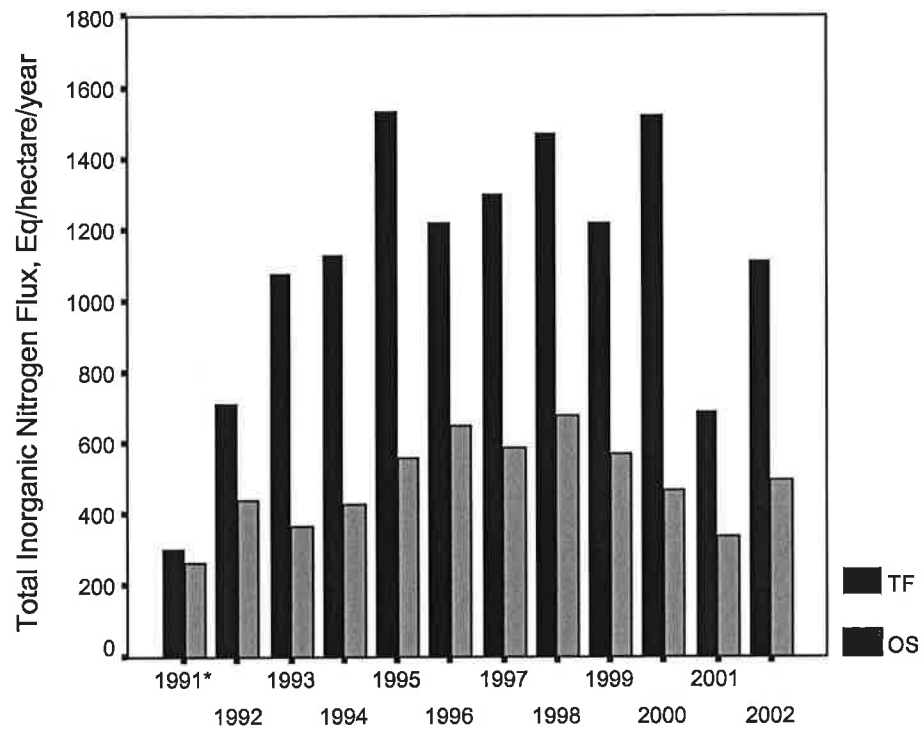


Figure 1-1. Total inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation. *The collections in 1991 started in June, and represent only half of the years total deposition rates.

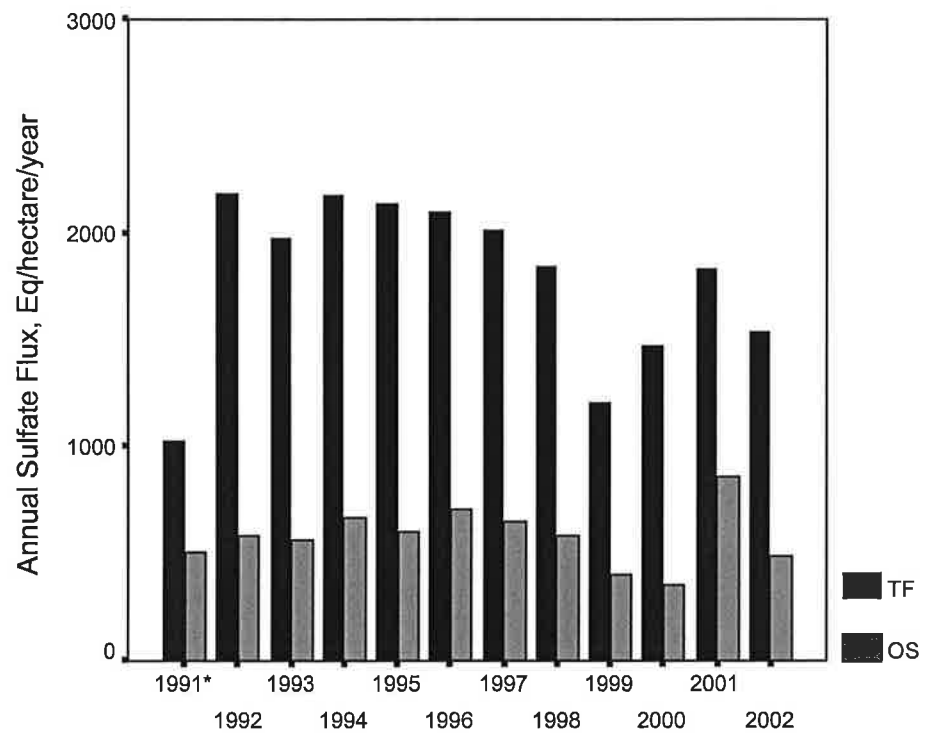


Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation. *The collections in 1991 started in June, and represent only half of the years total deposition rates.

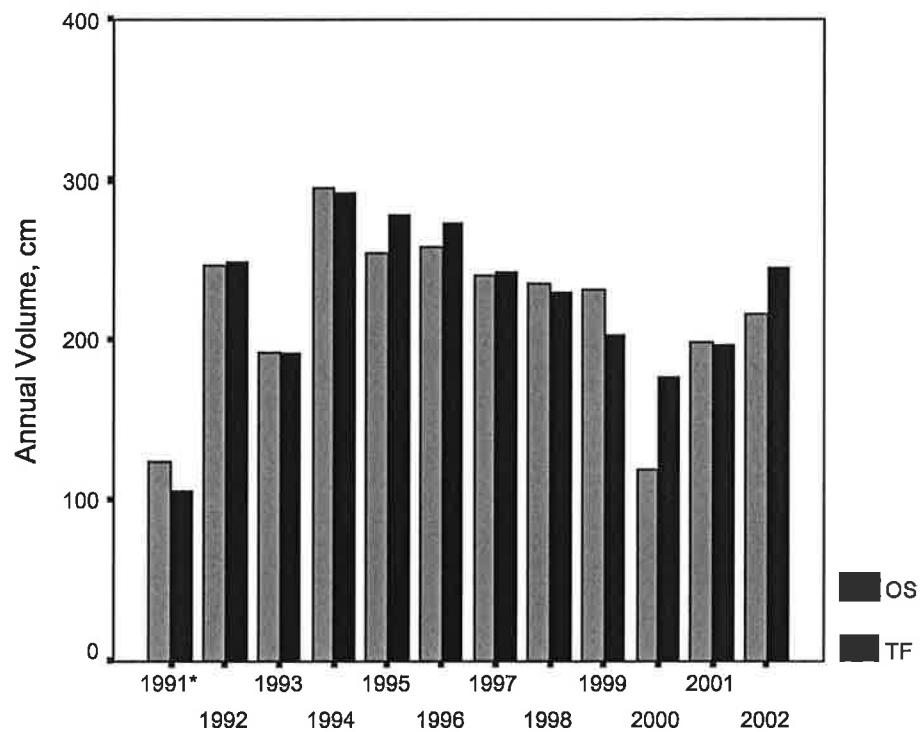


Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW. *The collections in 1991 started in June, and represent only half of the total deposition rates.

1.2 Soil Lysimeter Chemistry

Soil water chemistry is collected monthly from 12 lysimeters located at 3 different depths within the NDW. The annual volumes for the upper, middle, and lower lysimeters were 7645, 9426, and 17288 mL, respectively. Statistical summaries of the data can be found in Tables 1-1, 1-2, and 1-3.

Table 1-1. Statistical summaries for pH and conductivity from the soil lysimeters.

		pH	Conductivity, $\mu\text{S}/\text{cm}^2$
Upper Lysimeter	Minimum	3.50	29.4
	Average	4.10	65.18
	Maximum	4.53	168.20
Middle Lysimeter	Minimum	3.99	30.40
	Average	4.28	42.45
	Maximum	4.60	55.80
Lower Lysimeter	Minimum	4.27	30.00
	Average	4.53	42.13
	Maximum	5.37	102.90

Table 1-2. Statistical summaries of the anion chemistry analysis on the soil lysimeter samples. All values are given in $\mu\text{eq}/\text{L}$.

		Cl^-	NO_3^-	SO_4^{2-}
Upper Lysimeter	Minimum	8.04	45.47	60.85
	Average	36.16	191.40	107.48
	Maximum	195.13	784.94	316.93
Middle Lysimeter	Minimum	10.77	35.87	58.50
	Average	22.04	96.01	88.41
	Maximum	33.32	137.63	103.33
Lower Lysimeter	Minimum	6.83	50.23	78.37
	Average	20.41	103.70	84.76
	Maximum	35.83	167.40	107.04

Table 1-3. Statistical summaries of the cation chemistry analysis on the soil lysimeter samples. All values are given in $\mu\text{eq/L}$.

		Na⁺	K⁺	Mg²⁺	Ca²⁺
Upper Lysimeter	Minimum	20.88	3.69	2.39	19.65
	Average	76.80	16.07	41.67	87.99
	Maximum	482.62	41.20	249.38	577.50
Middle Lysimeter	Minimum	19.80	0	2.22	14.45
	Average	28.26	5.58	18.92	28.80
	Maximum	43.73	11.67	27.16	52.85
Lower Lysimeter	Minimum	10.39	2.42	14.40	15.35
	Average	23.41	5.58	27.09	48.22
	Maximum	28.47	9.95	41.15	216.50

1.3 Analyzed Summary of 2002 Meteorological Data for the Noland Divide Watershed

The meteorological data for the Noland Divide Watershed has been reviewed and analyzed. The data will be presented by category. Graphical representation and descriptive statistics will be included along with brief analysis of the data.

1.3.1 Data Lapse

In each category of data, there will be a lapse in data from March 11 to April 6 (Julian Day 70-96) and September 18 to October 14 (Julian Day 261-287). The unavailability of data is due to equipment malfunctions and failures.

1.3.2 Air Temperature

As expected, the air temperature is the lowest at the beginning of the year and at the end (Figure 1-4). At the end of May, the average air temperature begins to increase and then becomes fairly steady around the beginning of July. The average air temperature then begins to decrease about the middle of August. This trend is very similar for the daily maximum and daily minimum air temperatures. Statistical parameters are summarized in Table 1-4.

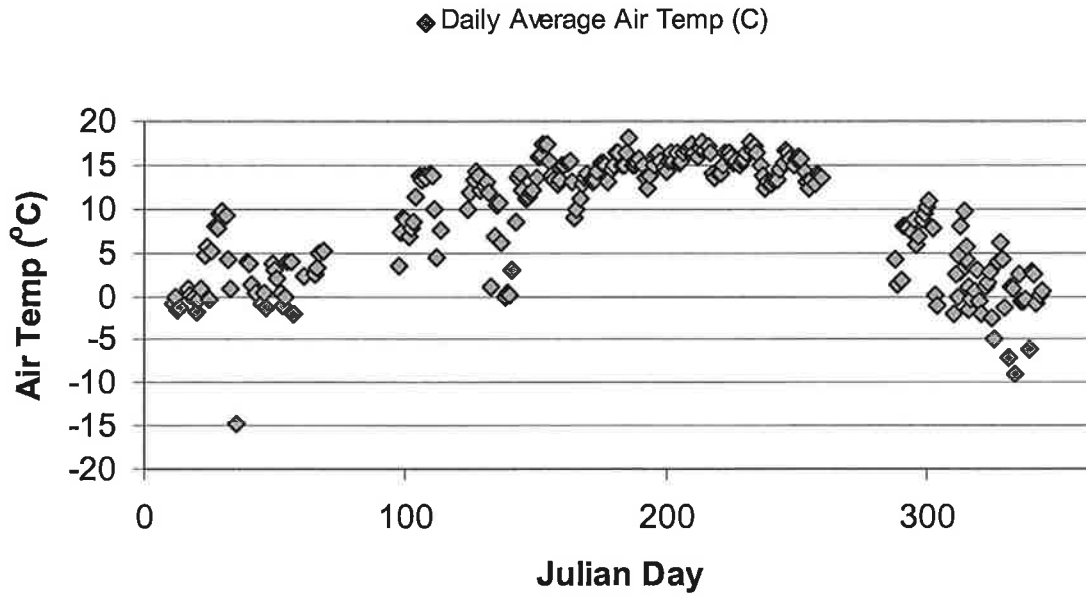


Figure 1-4. Daily average air temperature measured at the Noland Divide Watershed

Table 1-4. Statistical summary air temperature for Noland Divide Watershed

Parameters	Daily Average Air Temp (°C)	Daily Max Air Temp (°C)	Daily Min Air Temp (°C)
Mean	9.031	13.202	5.890
Standard Error of Mean	0.418	0.433	0.459
Median	11.595	15.23	8.775
Standard Deviation	6.669	6.921	7.316
Range	32.66	28.787	30.92
Minimum	-14.67	-4.897	-15.51
Maximum	17.99	23.89	15.38
Count	254	256	254

1.3.3 Wind direction

The wind data was grouped based on the direction in which it originated from (Figure 1-5). As the pie chart shows, wind direction originates from the southeast 63% of the time.

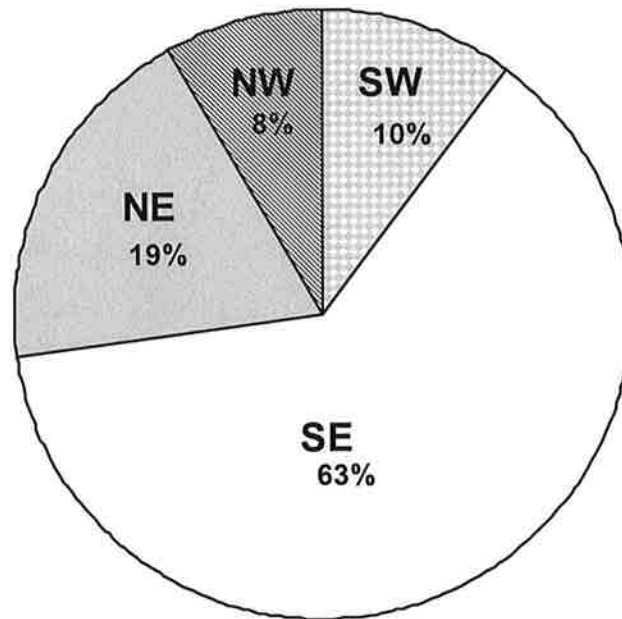


Figure 1-5. Percent wind direction for Noland Divide Watershed

1.3.4 Wind Speed

Wind speed varied throughout the year and had a daily average value of 7.65 miles per hour. The maximum speed recorded in 2002 was 57.1 miles per hour and occurred on November 8th.

1.3.5 Relative Humidity

The maximum relative humidity is typically near 100% except during the coldest times of the year (Figure 1-6). The minimum humidity varied throughout the year, but tended to be higher in the summer as shown in Figure 1-6.

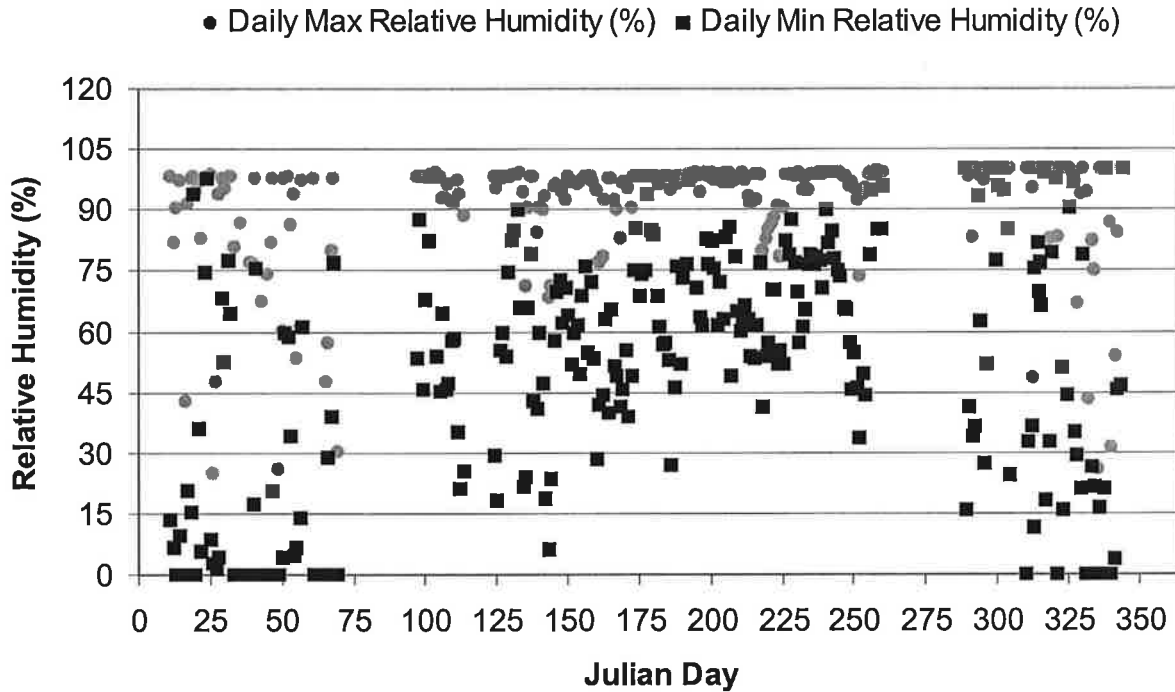


Figure 1-6. Relative humidity for the Noland Divide Watershed

1.3.6. Solar Radiation

Due to equipment failure, much of the data for solar radiation was not available. Based on the available data, the radiation flux increased during the summer as expected.

1.3.7 Soil Water Content

The soil water increases presumably due to rain events, and then decreases (Figure 1-7). The upper soil water content tends to vary more. This is most likely due to its closer position to the surface, which makes it dry at quicker rate.

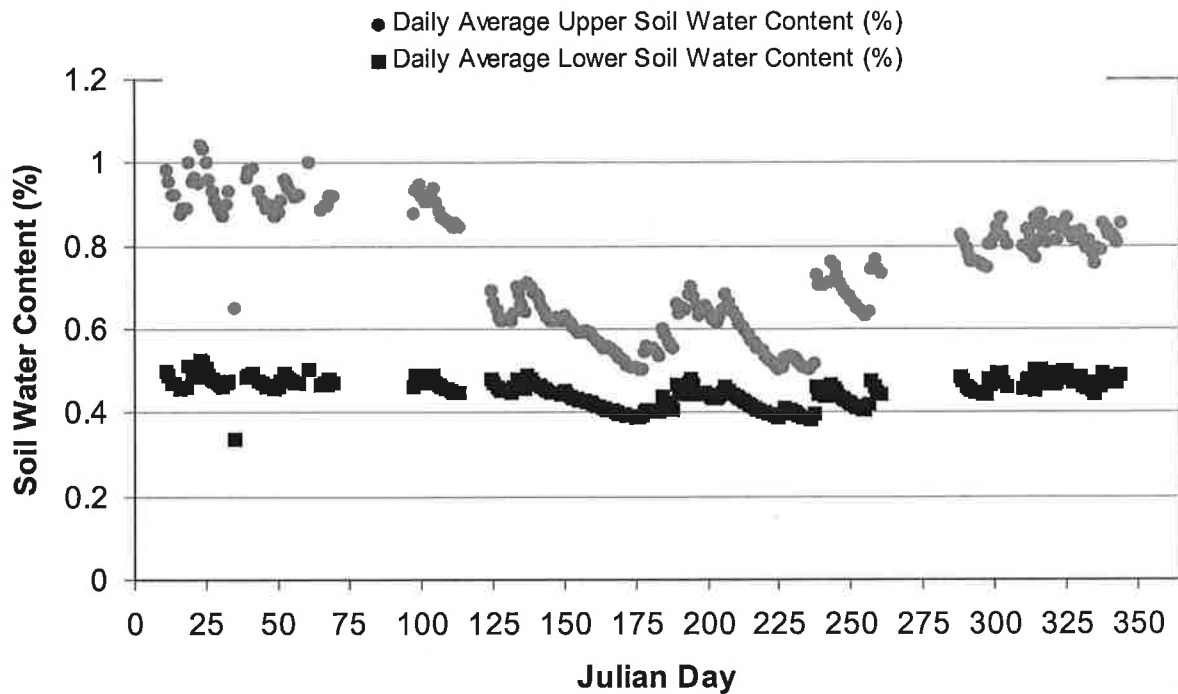


Figure 1-7. Soil water content for Noland Divide Watershed

1.3.8 Soil Temperature

Soil temperature is undoubtedly related to air temperature but has much less variability (Figure 1-8). An increase in soil temperature can be seen during the summer months. The lower soil temperature has a narrower range most likely due to the insulation the top layer of soil adds. The upper soil temperature is higher than lower soil temperature during the summer and lower during the winter. This can be attributed again to insulation.

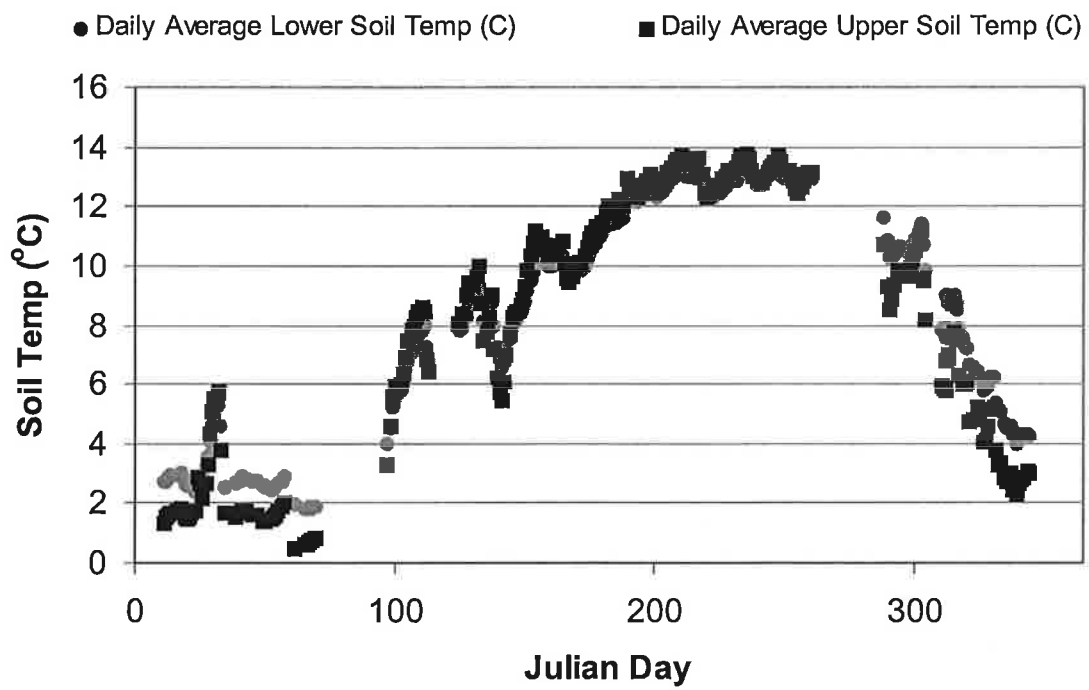


Figure 1-8. Soil temperature for Noland Divide Watershed

2. Stream Survey Results

The following analyses utilize the chemistry data of collected samples from ninety sites within the GRSM. The data set includes samples collected during the four stream surveys in March, May, August, and November, 2002. Throughout the following text, comparisons will be made between the data collected in 2002 and previous data collected from October, 1993 to November, 2001.

The median water constituent values for each sampling location are shown in table 2-1 for the year 2002. Table 2-2 shows the percent change in median water quality values of the 2002 data from the 1993-2001 data. For the most part, percent changes are fairly small. There are some large percent changes in acid neutralizing capacity for several sites, but these sites generally have very low ANC values which can cause large percent changes with little variation.

Table 2-3 shows descriptive statistics of the water quality constituents for the year 2002. The descriptive statistics are applied to the set of median water quality values for each sampling site. These values are quite similar to the values obtained for the 1993-2001 data set.

Stream water pH is one of the most important water quality parameters measured in the GRSM. It is a good indicator of the stream health, which includes the stream's ability to sustain aquatic life. Table 2-4 lists several pH ranges, potential biological effects, and the percentage of sample sites with median pH within those ranges for the 2002 and 1993-2001 data sets although the reader should understand that many of the low pH streams are too small to support trout, that seven sites are springs, and that many other factors are also important for aquatic organisms. The percentages of sampling sites within each range for the 2002 data changes very little from the 1993-

2001 data set.

Figure 2-1 is a scatter plot of median pH values for the 2002 and 1993-2001 data plotted by elevation. The plot also shows that overall median pH values changed very little as evidenced by similar slopes for the fitted lines.

Table 2-1. Median water quality values

Site ID	Elev. (ft)	Elev. (m)	pH	ANC (µeq/L)	Conductivity (µS/cm)	Chloride (µeq/L)	Nitrate (µeq/L)	Sulfate (µeq/L)	Sodium (µeq/L)	Potassium (µeq/L)	Magnesium (µeq/L)	Calcium (µeq/L)
1	2200	671	6.17	38.04	16.07	11.46	27.59	43.66	35.76	10.58	19.05	54.63
3	1675	1675	6.55	67.91	17.02	13.66	11.61	29.63	53.97	9.96	23.05	43.80
4	2080	634	6.50	75.28	14.64	9.10	3.33	17.04	53.56	10.92	24.73	45.85
13	1100	335	6.77	89.92	17.65	14.50	6.05	33.26	45.60	13.23	28.19	61.23
14	1140	347	6.80	75.60	15.55	11.43	5.36	31.73	41.66	9.82	28.15	64.30
20	1700	518	7.10	100.80	17.41	21.58	0.00	28.39	46.71	14.43	28.64	78.15
23	1150	351	6.25	43.46	13.55	13.41	8.61	29.85	42.46	11.37	26.79	49.88
24	1150	351	6.46	92.32	18.45	15.52	2.99	41.83	54.61	12.27	40.70	93.28
30	1430	436	6.23	28.58	20.90	16.34	27.23	63.68	33.03	7.81	38.97	73.35
34	1960	597	6.35	46.23	13.42	12.78	8.71	30.50	34.07	9.63	22.96	55.63
43	2340	713	5.76	5.89	17.62	12.79	22.57	69.52	27.40	8.06	37.98	57.70
45	3200	975	5.47	-0.52	21.00	14.40	32.00	94.84	24.39	4.58	50.21	71.83
46	2750	838	5.45	0.04	18.51	13.19	22.81	82.00	26.51	4.08	36.63	56.48
47	2400	732	6.01	12.98	12.70	11.09	17.94	39.00	24.49	8.85	21.69	42.03
49	1670	509	6.14	19.63	16.20	10.95	21.41	56.38	30.42	7.42	35.35	58.88
50	1665	507	6.18	21.91	15.83	11.73	24.92	48.69	33.63	10.47	28.93	56.80
52	1350	411	6.16	34.15	16.08	13.59	21.98	47.08	35.18	8.66	30.08	66.25
66	2680	817	6.14	20.24	20.30	14.06	32.04	73.02	29.50	7.03	38.68	88.10
71	3400	1036	5.78	26.84	15.60	13.15	35.04	41.30	26.96	8.54	26.83	66.05
73	3360	1024	5.92	19.92	20.10	16.45	31.48	84.12	24.06	4.99	43.21	92.60
74	3820	1164	6.16	18.37	22.70	15.83	31.66	92.83	24.17	5.21	46.09	102.70
103	4330	1320	5.43	-3.38	18.72	15.97	49.12	64.09	34.87	10.21	20.78	64.70
104	4200	1280	5.57	1.38	17.60	15.34	55.12	50.97	33.12	16.76	19.30	57.48
106	3840	1170	5.94	11.95	17.34	12.49	43.47	55.15	30.74	12.72	22.14	81.35
107	3040	927	6.09	13.71	16.19	11.50	35.38	49.99	31.17	10.06	19.38	66.88
114	2510	765	6.32	28.86	17.70	12.51	34.87	46.41	39.25	8.73	35.60	70.68
115	3840	1170	6.30	34.27	18.43	14.18	31.89	52.18	40.88	8.66	39.55	75.50
127	2980	908	6.50	42.72	11.81	12.33	13.54	19.64	36.97	11.18	16.79	34.60
137	2750	838	6.09	27.98	16.64	12.72	28.53	46.11	34.58	8.10	25.72	53.28
138	3470	1058	5.68	5.89	14.17	15.24	31.99	36.94	30.86	7.52	18.15	43.93
142	3300	1006	6.57	46.47	10.23	12.74	5.96	19.03	36.37	10.61	15.47	35.33
143	3280	1000	6.52	43.99	10.12	12.49	5.33	18.44	34.77	9.35	15.80	35.55
144	2990	911	6.52	50.63	10.26	7.64	5.25	18.37	35.46	9.32	15.47	32.58
147	2460	750	6.59	72.95	13.84	13.93	9.95	21.45	47.44	11.91	23.37	43.85
148	2475	754	6.76	117.08	15.85	10.33	0.00	20.35	71.25	14.37	26.54	53.10
149	2550	777	6.66	64.44	13.58	12.05	7.83	21.35	48.73	10.84	23.95	47.28
150	2620	799	6.66	65.68	13.72	15.02	10.19	20.95	46.63	11.40	22.26	45.80
156	1110	338	7.05	293.34	36.10	16.68	1.65	40.01	50.75	11.07	73.66	241.75
173	1715	523	6.76	115.60	24.45	14.76	6.43	25.33	47.36	11.53	31.28	82.03
174	1715	523	6.94	711.93	72.80	18.50	9.22	41.44	56.58	15.58	96.58	499.50
183	4280	1305	6.10	42.11	9.49	10.96	2.59	7.93	32.35	6.41	11.03	23.00
184	2830	863	6.43	35.91	12.24	16.21	21.51	19.72	35.48	9.50	16.38	42.05
186	1965	599	6.50	38.44	12.38	16.15	17.86	27.85	40.54	12.40	21.56	48.60
190	2120	646	6.56	52.80	12.79	12.78	12.19	28.68	32.31	7.72	18.02	42.35
191	3200	975	6.22	11.22	10.99	13.31	12.48	25.97	28.66	7.55	16.21	37.20
192	3200	975	5.90	6.92	13.75	12.74	21.27	38.87	29.37	6.13	23.54	50.65

Table 2-1 cont. Median water quality values

Site ID	Elev. (ft)	Elev. (m)	pH	ANC (µeq/L)	Conductivity (µS/cm)	Chloride (µeq/L)	Nitrate (µeq/L)	Sulfate (µeq/L)	Sodium (µeq/L)	Potassium (µeq/L)	Magnesium (µeq/L)	Calcium (µeq/L)
193	1920	585	6.48	31.14	11.03	12.79	5.71	25.45	33.72	9.17	18.77	41.45
194	1700	518	6.32	28.97	12.19	12.37	8.32	28.70	34.47	8.29	20.45	37.15
195	4810	1466	5.70	27.15	7.57	12.72	0.00	11.01	28.66	6.54	9.55	17.20
200	3320	1012	6.33	20.21	13.01	12.10	33.16	24.88	35.32	9.75	16.13	44.20
201	4800	1463	5.88	32.38	8.80	9.41	6.15	14.02	23.88	8.62	12.84	26.65
209	2700	823	6.55	38.07	9.92	12.00	0.00	23.14	36.76	10.22	16.54	25.85
210	2740	835	6.52	34.44	15.11	12.52	18.90	36.63	35.02	10.27	22.43	60.00
213	3340	1018	6.06	4.70	11.35	16.99	22.68	29.13	28.63	8.39	18.48	31.25
214	3440	1049	6.21	22.56	10.77	13.94	15.11	22.86	34.17	9.56	16.46	25.88
215	3380	1030	6.48	46.73	12.54	12.10	9.22	34.59	38.89	10.20	26.26	50.00
218	5440	1658	5.28	-9.08	22.90	23.50	76.06	43.08	35.00	17.40	25.02	44.53
219	5510	1679	5.03	0.90	25.15	22.32	70.54	60.95	37.76	15.71	24.40	46.88
220	5500	1676	5.61	5.99	16.70	12.87	59.62	31.13	29.44	12.86	22.06	49.25
221	4000	1219	6.31	28.80	11.12	11.92	27.59	14.15	31.40	9.11	17.45	33.15
233	4255	1297	5.57	3.49	24.85	16.17	33.29	106.84	24.52	4.54	50.86	102.65
234	5000	1524	5.80	6.08	15.25	16.39	48.30	29.44	37.25	10.47	24.20	45.60
237	4520	1378	4.77	-18.06	22.85	13.55	29.49	76.18	21.07	3.57	33.21	50.33
251	4010	1222	6.13	20.16	33.20	17.23	37.11	185.35	42.45	10.00	87.24	127.55
252	4680	1426	5.88	13.40	38.65	15.07	52.59	196.84	49.70	9.68	97.94	124.35
253	4760	4760	6.59	82.59	23.35	17.28	52.79	39.11	52.11	8.61	43.62	96.58
266	2015	614	6.58	70.76	13.01	10.94	4.68	29.17	42.57	11.60	23.37	43.95
268	2185	666	6.50	48.30	13.82	11.40	9.79	30.62	39.71	7.89	25.19	45.25
291	5260	1603	6.22	22.68	11.95	14.04	29.43	23.87	33.68	8.36	17.28	36.40
293	2755	840	6.58	61.40	15.46	16.81	16.09	23.61	49.38	12.26	28.56	51.45
310	2240	683	6.57	71.94	13.04	13.00	4.12	19.25	40.57	9.45	21.48	40.60
311	2155	657	6.56	58.30	11.44	12.92	2.35	16.08	38.21	9.66	19.09	36.05
336	4760	1451	6.47	48.16	11.57	13.96	23.11	9.26	38.12	11.04	20.45	35.40
337	4740	1445	6.43	38.63	11.81	11.28	25.55	17.17	36.56	9.11	20.86	34.53
472	2200	671	6.18	22.41	12.05	10.95	10.48	32.74	34.55	7.55	19.42	43.95
473	3630	1106	6.27	32.34	22.90	15.16	31.91	83.58	25.22	5.03	41.56	88.35
474	2400	732	6.54	51.90	13.31	12.57	17.79	33.07	31.66	9.13	21.73	50.15
475	2950	899	6.48	53.03	12.75	14.12	17.82	27.57	36.93	8.87	19.59	39.83
479	1740	530	6.52	64.15	11.21	16.10	2.23	16.36	40.95	10.43	19.63	38.78
480	2185	666	6.62	77.92	13.61	12.85	0.00	21.12	44.67	11.75	25.88	44.53
481	2540	774	6.34	70.69	19.50	12.24	0.00	61.18	45.10	15.31	41.15	54.90
482	2540	774	6.60	79.88	14.25	12.83	3.02	19.71	46.55	11.74	35.19	46.78
483	2320	707	6.64	75.01	15.18	12.95	0.00	31.69	47.35	12.21	33.58	47.15
484	2475	754	6.56	49.76	10.26	12.85	2.90	15.18	34.77	9.11	16.91	33.70
485	2860	872	6.45	63.02	11.74	13.38	0.00	14.61	41.88	10.37	20.91	41.10
488	1790	546	6.43	37.15	11.71	16.26	6.32	23.39	38.82	8.28	18.68	36.83
489	1710	521	7.41	728.65	73.45	17.58	9.18	41.75	56.72	13.04	150.21	693.25
492	2730	832	6.19	39.62	17.68	16.00	40.67	45.45	43.51	9.28	32.63	63.65
493	2840	866	6.45	55.21	12.75	11.11	8.50	18.17	42.22	10.19	17.61	37.75

Table 2-2. Percentage change in 2002 median water quality values from 1993-2002 data

Site ID	Elev. (ft)	Elev. (m)	pH	ANC	Conductivity	Cl	NO ₃	SO ₄	Na	K	Mg	Ca
1	2200	671	-1.07%	7.76%	4.32%	-16.90%	12.45%	-6.92%	2.80%	-9.87%	-5.89%	-16.51%
3	1675	1675	0.90%	-7.23%	9.49%	5.98%	-31.39%	-15.09%	14.32%	-0.57%	-22.44%	-31.35%
4	2080	634	2.65%	25.39%	5.17%	-25.88%	-44.70%	-30.30%	14.93%	0.03%	5.81%	-15.87%
13	1100	335	2.47%	-18.31%	2.14%	-1.75%	-6.18%	-4.49%	10.67%	7.13%	-20.72%	-17.87%
14	1140	347	2.82%	-26.00%	-8.77%	-21.79%	-18.65%	-8.38%	0.49%	-27.27%	-12.08%	-13.34%
20	1700	518	9.22%	18.45%	13.05%	62.76%	-100.00%	-15.51%	18.68%	18.26%	8.41%	19.13%
23	1150	351	-4.79%	-55.80%	-15.42%	-13.33%	9.71%	-4.85%	16.52%	4.05%	-25.09%	-18.47%
24	1150	351	-3.51%	-36.48%	-18.00%	-1.48%	-44.53%	-1.21%	1.22%	-4.82%	-16.04%	-8.42%
30	1430	436	-3.29%	-51.98%	5.82%	-2.96%	8.64%	0.67%	-5.12%	-14.71%	-1.35%	-7.15%
34	1960	597	-1.22%	-28.06%	-5.86%	-29.38%	-18.08%	-6.61%	-4.98%	-18.94%	-5.26%	-7.41%
43	2340	713	-2.29%	-44.64%	11.13%	-4.11%	-6.96%	10.69%	6.35%	33.81%	23.07%	18.36%
45	3200	975	-1.76%	-113.95%	10.64%	-6.48%	1.27%	9.66%	9.35%	2.73%	22.00%	37.48%
46	2750	838	-5.48%	-99.26%	10.48%	-7.22%	-21.09%	13.21%	3.09%	-7.10%	1.60%	12.50%
47	2400	732	1.56%	17.47%	8.09%	-17.18%	-12.31%	-4.63%	-1.38%	-0.49%	26.68%	18.21%
49	1670	509	-1.83%	-50.09%	2.21%	-19.58%	24.80%	12.35%	-7.78%	0.40%	5.53%	-20.97%
50	1665	507	-2.36%	-43.35%	9.02%	-23.63%	43.85%	3.76%	-3.25%	20.97%	17.17%	2.34%
52	1350	411	-3.61%	-33.96%	3.54%	-4.03%	36.86%	-1.36%	-5.27%	4.52%	9.76%	7.29%
66	2680	817	-2.07%	-40.42%	6.39%	-6.10%	-0.37%	5.04%	15.86%	6.83%	-1.26%	14.79%
71	3400	1036	-6.62%	3.03%	-0.89%	-11.55%	9.82%	-7.76%	-3.81%	2.81%	-5.78%	-2.94%
73	3360	1024	-6.39%	-36.46%	1.01%	1.94%	-5.39%	7.22%	3.23%	-1.26%	-1.50%	19.91%
74	3820	1164	-4.02%	-65.54%	-4.62%	2.03%	-7.48%	3.27%	-1.65%	9.91%	-16.42%	-15.82%
103	4330	1320	-3.08%	-256.25%	-4.56%	10.84%	0.82%	-4.67%	21.04%	-5.76%	-1.37%	-16.19%
104	4200	1280	-1.89%	-65.59%	-2.63%	9.54%	10.50%	-8.64%	17.89%	35.37%	-6.20%	-19.78%
106	3840	1170	-1.03%	-26.56%	-0.43%	-15.20%	5.71%	-5.11%	10.04%	-3.40%	0.75%	1.06%
107	3040	927	0.78%	-30.03%	0.81%	-3.42%	3.22%	-6.37%	13.46%	-12.19%	-1.46%	-2.80%
114	2510	765	0.73%	-21.39%	4.33%	-19.47%	-10.86%	3.67%	7.71%	-5.28%	6.00%	10.17%
115	3840	1170	1.80%	-7.69%	15.52%	-16.11%	10.78%	8.52%	25.04%	8.85%	13.33%	19.41%
127	2980	908	1.56%	-8.20%	5.45%	-21.16%	-7.16%	1.22%	-3.50%	0.02%	-12.45%	-6.23%
137	2750	838	3.62%	137.12%	14.53%	-6.93%	-8.87%	-10.94%	13.88%	-3.20%	-5.59%	-1.52%
138	3470	1058	2.65%	95.72%	3.28%	0.37%	-8.54%	-1.51%	10.27%	-15.66%	-2.43%	3.11%
142	3300	1006	1.68%	-18.08%	-6.27%	-5.48%	-19.11%	25.50%	0.88%	-10.93%	-12.96%	-8.01%
143	3280	1000	1.71%	-9.36%	-5.29%	-13.30%	-34.35%	-11.41%	-10.53%	-13.81%	-4.00%	2.89%
144	2990	911	1.18%	-7.27%	-3.98%	-43.91%	-23.90%	4.78%	-7.83%	-19.94%	-12.15%	-13.02%
147	2460	750	-0.14%	-15.29%	-5.40%	-3.03%	24.43%	0.59%	-4.00%	-16.59%	-12.07%	-16.56%
148	2475	754	1.33%	-8.47%	-5.43%	-30.88%	-100.00%	5.14%	2.33%	-8.60%	-14.46%	-19.05%
149	2550	777	1.72%	-19.88%	-1.63%	-18.17%	-4.82%	0.34%	-2.94%	-26.03%	-10.74%	-4.78%
150	2620	799	1.92%	-17.06%	2.43%	-3.04%	12.05%	1.65%	-5.57%	-16.44%	-12.46%	-9.31%
156	1110	338	-2.63%	-42.10%	-26.10%	-19.85%	-45.06%	-7.92%	-7.21%	-32.15%	-37.41%	6.66%
173	1715	523	1.47%	12.90%	44.67%	-14.75%	20.46%	-3.41%	4.95%	-3.21%	-15.93%	31.24%
174	1715	523	-6.28%	-35.06%	-29.66%	-15.97%	-24.79%	-19.33%	1.98%	-3.71%	-57.33%	-53.21%
183	4280	1305	7.01%	14.76%	4.23%	-24.52%	-48.61%	-8.68%	5.37%	2.60%	8.50%	42.19%
184	2830	863	3.68%	14.91%	-5.00%	-14.77%	-17.24%	-28.35%	-8.96%	-15.56%	-6.57%	-9.38%
186	1965	599	2.30%	-19.29%	-5.35%	-2.38%	2.38%	-4.10%	-1.22%	9.22%	10.08%	5.65%
190	2120	646	5.09%	82.57%	9.60%	-7.76%	-24.51%	-8.21%	1.07%	-7.16%	1.39%	6.81%
191	3200	975	1.62%	-45.23%	4.52%	-14.08%	-36.03%	-1.83%	-3.10%	-17.55%	7.65%	5.53%
192	3200	975	-3.41%	-68.91%	8.61%	-5.95%	-4.10%	-6.22%	13.32%	-6.74%	0.35%	0.30%

Note: A negative % change indicates a decrease in 2002 median values from previous data

Table 2-2 cont. Percentage Change in 2002 Median Water Quality Values from 1993-2002 Data

Site ID	Elev. (ft)	Elev. (m)	pH	ANC	Conductivity	Cl	NO ₃	SO ₄	Na	K	Mg	Ca
193	1920	585	1.54%	-41.99%	-3.29%	-12.88%	-24.70%	7.65%	-5.79%	-6.90%	-8.80%	7.11%
194	1700	518	-0.11%	-35.89%	6.89%	-21.73%	-18.25%	1.59%	0.60%	-10.72%	-3.31%	-10.27%
195	4810	1466	-1.21%	-6.73%	0.26%	-14.83%	-100.00%	33.89%	15.18%	10.66%	1.75%	-1.99%
200	3320	1012	3.38%	-26.36%	4.67%	-30.35%	25.84%	-7.53%	4.30%	-9.26%	-1.01%	3.63%
201	4800	1463	2.64%	-5.78%	-17.68%	-25.62%	-51.32%	-7.59%	-12.64%	-10.26%	-1.89%	-18.00%
209	2700	823	4.98%	15.38%	0.66%	-13.72%	-100.00%	-5.75%	10.96%	5.59%	2.03%	-9.30%
210	2740	835	2.02%	-30.77%	7.13%	-0.02%	36.11%	-7.20%	8.30%	-1.91%	0.18%	-2.56%
213	3340	1018	-0.74%	-77.65%	1.48%	23.43%	11.65%	-1.19%	-0.31%	1.03%	-5.67%	-10.39%
214	3440	1049	-1.31%	-40.33%	-2.00%	-12.86%	7.89%	-0.17%	5.61%	-4.06%	-7.83%	-24.12%
215	3380	1030	1.74%	-5.95%	-5.89%	-21.28%	-25.35%	0.13%	5.98%	9.35%	2.90%	-0.70%
218	5440	1658	4.88%	-471.56%	9.05%	35.53%	52.24%	-25.64%	31.14%	30.07%	-3.18%	1.66%
219	5510	1679	2.69%	-175.31%	5.45%	43.10%	-11.37%	1.92%	45.69%	22.91%	14.48%	-11.18%
220	5500	1676	5.84%	76.29%	0.57%	3.88%	3.87%	0.58%	13.02%	9.03%	6.35%	-3.05%
221	4000	1219	2.12%	9.50%	8.07%	-21.70%	12.36%	-14.54%	-2.41%	0.65%	3.17%	13.43%
233	4255	1297	-9.28%	-88.67%	8.28%	-4.52%	-2.76%	-0.13%	3.45%	7.09%	-7.07%	0.64%
234	5000	1524	-1.45%	-65.08%	-2.21%	-2.36%	-15.49%	6.89%	9.60%	72.11%	-11.04%	-6.70%
237	4520	1378	-1.04%	26.64%	15.81%	1.08%	-12.83%	8.14%	18.16%	10.34%	0.87%	5.17%
251	4010	1222	0.53%	-6.41%	7.10%	-3.66%	-0.88%	8.80%	-3.23%	-5.31%	7.61%	7.73%
252	4680	1426	17.38%	-572.56%	-8.63%	-13.60%	-2.98%	-35.47%	1.33%	-19.62%	36.78%	13.46%
253	4760	4760	2.44%	-1.02%	-0.64%	-10.14%	-6.82%	-5.42%	-4.62%	-6.15%	-6.19%	0.60%
266	2015	614	0.98%	-0.69%	-4.90%	-30.21%	-17.88%	13.34%	-2.50%	-4.94%	0.00%	-5.48%
268	2185	666	1.12%	-25.67%	5.34%	-21.92%	16.09%	5.86%	-5.63%	-29.12%	0.00%	-9.23%
291	5260	1603	1.88%	-9.97%	-4.78%	-12.97%	-17.24%	1.82%	-7.54%	-18.81%	-10.64%	-15.94%
293	2755	840	0.43%	-26.92%	-3.65%	6.45%	-10.66%	-1.56%	-6.77%	-10.26%	-9.64%	-11.06%
310	2240	683	1.36%	0.75%	9.81%	-16.09%	5.33%	-9.14%	-0.07%	-7.64%	-15.53%	-13.71%
311	2155	657	1.20%	-8.55%	-3.09%	-10.92%	-48.76%	-6.81%	-6.35%	-11.00%	-12.45%	-9.76%
336	4760	1451	1.69%	1.34%	2.80%	-15.12%	-8.54%	2.10%	-3.11%	-10.47%	1.02%	3.06%
337	4740	1445	2.56%	-8.09%	-0.80%	-27.37%	-3.71%	2.36%	-1.66%	-12.71%	-1.36%	-4.23%
472	2200	671	0.13%	-23.78%	3.88%	-29.19%	-30.53%	0.11%	6.85%	-11.38%	-11.28%	1.97%
473	3630	1106	1.52%	15.69%	12.81%	-12.43%	-0.40%	2.49%	8.33%	-7.92%	-9.42%	2.73%
474	2400	732	3.71%	-0.05%	2.35%	-14.35%	44.99%	1.74%	-10.06%	-14.79%	3.53%	2.35%
475	2950	899	2.68%	50.13%	10.87%	-18.52%	13.16%	-3.87%	15.97%	-15.18%	-4.42%	-1.67%
479	1740	530	0.92%	-6.91%	-8.16%	8.76%	-39.44%	-8.90%	-0.92%	-9.50%	-10.67%	-5.77%
480	2185	666	1.80%	-3.17%	1.99%	-10.25%	-100.00%	-1.11%	-2.73%	-4.03%	-7.50%	-3.10%
481	2540	774	-2.24%	-19.84%	15.04%	-13.38%	0.00%	22.65%	5.39%	18.48%	-9.09%	3.58%
482	2540	774	1.79%	-5.70%	8.45%	-14.00%	25.26%	-6.73%	2.61%	2.95%	1.54%	6.31%
483	2320	707	1.99%	-14.36%	6.53%	-14.57%	0.00%	9.81%	-0.63%	-8.16%	0.99%	-1.00%
484	2475	754	2.33%	-6.31%	-2.29%	-16.33%	-59.49%	-8.09%	-4.23%	-10.02%	-10.26%	-6.26%
485	2860	872	-0.54%	-9.37%	6.58%	-7.18%	-100.00%	1.35%	8.66%	-5.03%	-3.79%	4.98%
488	1790	546	0.57%	-16.10%	1.83%	-3.89%	-34.56%	2.37%	-1.09%	-18.86%	-3.81%	-1.93%
489	1710	521	-0.32%	-21.42%	-20.16%	-24.77%	-13.93%	-9.12%	-0.18%	-16.34%	-14.92%	-9.50%
492	2730	832	0.54%	41.25%	5.84%	3.57%	-10.67%	9.98%	26.98%	10.72%	-6.92%	4.82%
493	2840	866	-0.47%	-14.64%	5.37%	-23.12%	6.71%	2.09%	-6.49%	-14.98%	-6.96%	-10.55%

Note: A negative % change indicates a decrease in 2002 median values from previous data

Table 2-3. Descriptive statistics of 2002 median water quality values

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation
Median pH	4.77	7.41	6.27	0.44
Median ANC (µeq/L)	-18.06	728.65	57.44	108.30
Median Conductivity (mS/cm)	7.57	73.45	17.11	10.14
Median Chloride (µeq/L)	7.64	23.50	13.82	2.63
Median Nitrate (µeq/L)	0.00	76.06	19.57	17.08
Median Sulfate (µeq/L)	7.93	196.84	40.27	31.08
Median Sodium (µeq/L)	21.07	71.25	37.69	9.03
Median Ammonium (µeq/L)	0.00	0.00	0.00	0.00
Median Potassium (µeq/L)	3.57	17.40	9.80	2.71
Median Magnesium (µeq/L)	9.55	150.21	29.67	20.60
Median Calcium (µeq/L)	17.20	693.25	68.01	86.89

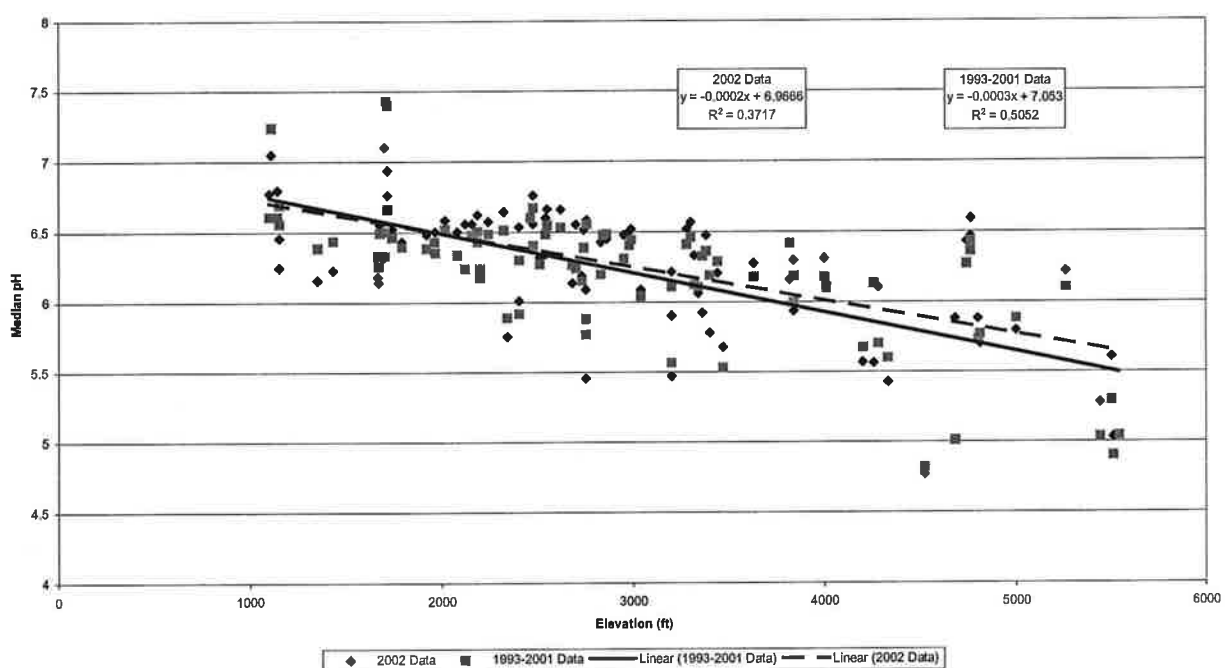


Figure 2.1. Median pH values by elevation

Table 2-4. pH effects and number of sampling sites by pH range

pH Range	Effects	% Sampling Sites 10/93 to 11/01	% Sampling Sites 3/02 to 11/02
7.5-6.0	Unlikely to be harmful unless a high runoff of acid, Al-rich water creates a mixing zone where $\text{Al}(\text{OH})_3$ precipitates causing acute toxicity.	71/90 = 78.9%	70/90 = 77.8%
6.0-5.0	Likely to be harmful to trout when Al concentrations exceed about 0.2 mg/l. The lower end of this range may be harmful to eggs, fry, and non-acclimated trout if calcium, sodium and chloride concentrations are low. Mechanisms: ionoregulatory dysfunction, respiratory stress.	17/90 = 18.9%	19/90 = 21.1%
5.0-4.5	Likely to be harmful to the eggs and fry, and to adults particularly in soft water containing low concentrations of sodium, calcium and chloride. Reduced reproduction, reduced growth, and abnormal behavioral patterns are likely in this range. Aluminum concentrations exceeding about 0.2 mg/l could increase the negative effects. Mechanisms: ionoregulatory dysfunction, respiratory stress, circulatory stress.	2/90 = 2.2%	1/90 = 1.1%
4.5-4.0	Likely that trout could not survive in this range for prolonged periods of time, although, natural populations of brown and brook trout have been found in this range. Reproduction in this range would be severely limited if not non-existent. Mechanisms: blood acidosis, ionoregulatory failure, respiratory failure, circulatory failure.	0/90 = 0.0%	0/90 = 0.0%
4.0-3.5	This range is likely to be acutely lethal to all salmonids.	0/90 = 0.0%	0/90 = 0.0%

3.0 Overall QA\QC Procedures

All procedures used to chemically analyze water samples are based upon standard published methods (Table 3-1). These procedures are used for the analysis of stream water, precipitation, and throughfall. Since the instruments and procedures are optimized for samples of low concentrations of dissolved constituents, dilution is used when necessary on higher concentration samples (*e.g.* throughfall). The samples are analyzed at room temperature to standardize the results among samples from different locations that may have been collected at different times and temperatures. Once pH, conductance, and ANC (Acid Neutralizing Capacity) have been obtained, samples are refrigerated until the other analysis are performed.

Table 3-1. Analytical procedures for chemistry analysis performed at the University of Tennessee.

Analysis	Procedure	Equipment	Method References
pH	Potentiometric	PC-Titration Plus	EPA Method 150.1
Conductance	Potentiometric	PC-Titration Plus	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus	Automated Gran Titration for low ionic strength waters, as in Hillman et al. 1986
Anions (NO_3^- , Cl^- , SO_4^{2-})	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Monovalent Cations (Na^+ , K^+ , NH_4^+)	Ion Chromatography	Dionex Ion Chromatograph	Manufacturers Protocols
Divalent Cations (Ca^{2+} , Mg^{2+})	Atomic Absorption	Instrumentation Laboratory	Standard Methods 3111 Manufacturers Protocols

3.1 Ion Chromatography QA\QC Procedures

Several QA\QC procedures are performed when running the IC. These procedures were developed to optimize the performance of the IC. The IC is fully automated. Once the samples are in the auto-sampler, the machine performs the analyses and the results are computed and placed in Excel spreadsheets. All deionized water used for standards and reagents are tested for conductivity before use. The deionized water must have a conductivity of less than 1.0 $\mu\text{S}/\text{cm}$. Some of the QA\QC samples include; reagent blanks, sample acidification blanks (for cations only since anion samples are not acidified), and replicates. Table 3-2 summarizes the results of the QA\QC procedures followed during the operation of the IC for anions. Table 3-3 summarizes the results of the procedures followed during the tests for monovalent cations using the IC. Both tables indicate

very good QA\QC procedures were followed during the analyses for anions and monovalent cations. In addition, a laboratory check sample is run with every set of IC analyses. Plotting the results of the multiple measurements made over time, insures cross comparisons of the results (Figure 3-1 and 3-2). Figure 3-1 shows multiple nitrate measurements during several different runs. Figure 3-2 shows multiple potassium measurements during several different runs. Both figures show very good precision with repeated measurements for those analytes.

Table 3-2. QA\QC results of the IC analysis for selected anions during a typical run.

QA\QC Procedure	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
R-squared of the calibration curve	0.994	0.996	0.995
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	0.23% (n=8)	0.57% (n=8)	0.39% (n=8)

Table 3-3. QA\QC results of the IC analysis for monovalent cations during a typical run.

QA\QC Procedure	Na ⁺	NH ₄ ⁺	K ⁺
R-squared of the calibration curve	0.991	0.994	0.996
Acidification blanks	not detected	not detected	not detected
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	10.04% (n=8)	5.22% (n=8)	9.53% (n=8)

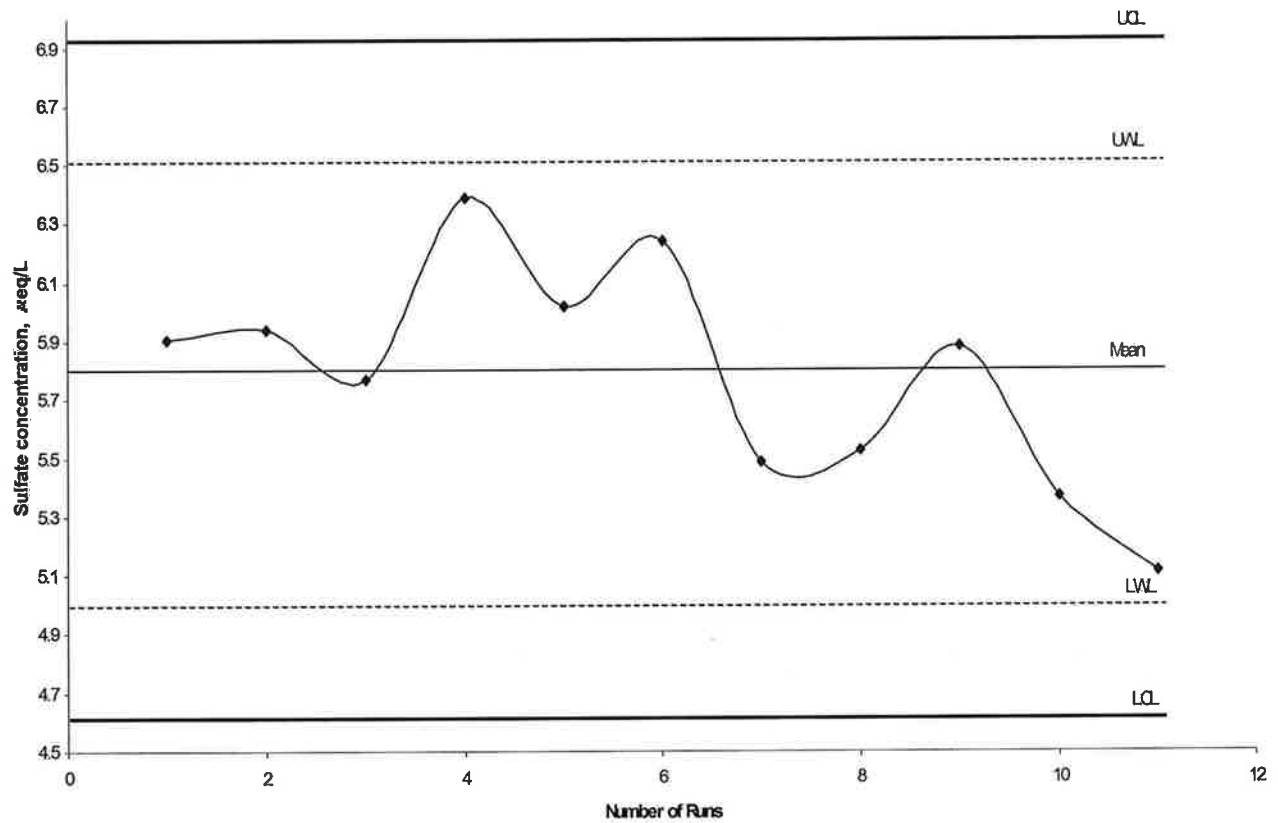


Figure 3-1. Sulfate concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (± 3 S.D.); UWL and LWL = upper and lower warning limits (± 2 S.D.).

3.2 Atomic Absorption QA\QC Procedures

A series of QA\QC samples were employed during the analysis and closely monitored throughout the entire run of samples. These procedures are outlined in detail in a protocols document previously developed by the current investigators. Some of the QA\QC samples include; reagent blanks, sample acidification blanks, replicates, and spiked samples. The sample acidification blanks and reagent blanks showed no traces of Mg or Ca. Therefore, the samples were not contaminated by the acidification process or the ionization suppressant (Table 3-4). Replicates and spiked samples were also analyzed. A spike sample is a procedure where a known concentration is added to a sample and the difference between the un-spiked and spiked sample is measured. The difference divided by the expected is the % recovery. Table 3-4 shows very good QA\QC results with respect to % spike recoveries very close to 100%. A quality control “check” sample is also used during the analysis. This sample is a prepared standard which is run after every 10 to 20 samples. If this sample differs more than 5 % from the expected, the machine is re-calibrated. The results of the “check” sample show very little drift of the instrument (Figure 3-3 and 3-4).

Table 3-4. Average QA\QC results of the AA analysis for magnesium and calcium.

QA\QC Procedure	Mg	Ca
R-squared of the calibration curve	0.9999	0.9998
Acidification blanks	not detected	not detected
Reagent blanks	not detected	not detected
Absolute average value of % spike recoveries	95.63% (n=5)	94.85% (n=4)

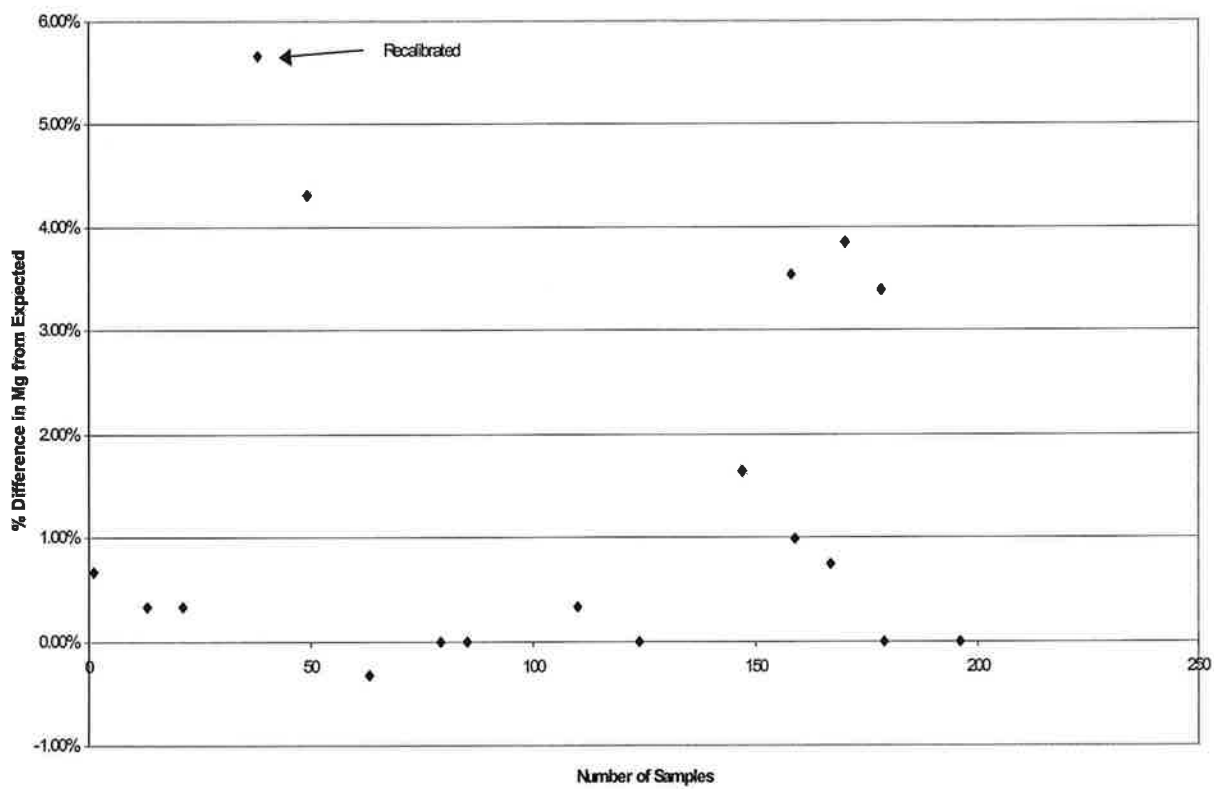


Figure 3-3. Magnesium standard check sample results plotted over the course of the analysis.

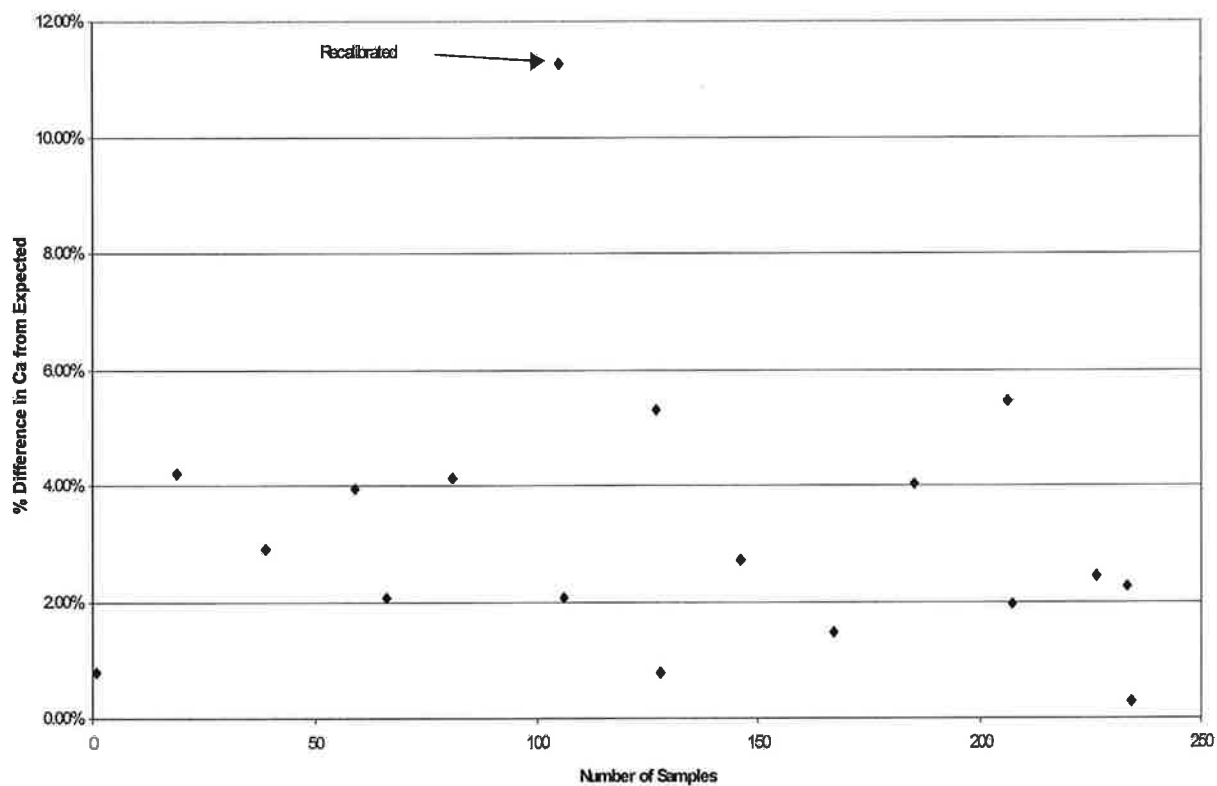


Figure 3-4. Calcium standard check sample results plotted over the course of the analysis.

3.3 Ion Balance

Once the all the analyses are performed, the results are entered into a spreadsheet and an ion balance or ion deficit for open site and throughfall is calculated as a final QA\QC procedure. An ion balance is calculated by summing up all the anions and cations in solution. This balance should be +/- 15 % according the US EPA recommend guidelines. Calculation of the ion balance is embedded in the Excel spreadsheets associated with each sampling site. Table 3-5 summarizes the results from both streamlets, along with the precipitation and throughfall measurements. The overall balance on all the sites is very close to zero, indicating good results have been obtained in the overall data.

Table 3-5. Average ion balances for both streamlets, precipitation and throughfall.

	NE Streamlet	SW Streamlet	Open Site	Throughfall
% Ion balance	2.14%	6.24%	18.93%	5.65%

3.4 Inter-laboratory Comparison Results

Once a year, the project participates in the fall analytical evaluation program operated by the United States Geological Survey (USGS). This program provides a variety of standard reference samples to accomplish quality assurance testing at USGS and non-USGS laboratories. A series of samples are prepared and distributed each spring and fall, we generally only participate in the fall comparisons. The program began in 1962 from a single sample that was prepared and sent to twenty-three USGS laboratories. Currently, there are 270 USGS and non-USGS laboratories enrolled in the program.

Though this is not a laboratory certification program, participation in this quality assurance program is mandatory for all laboratories providing water-quality data for USGS sponsored reports or storage in the USGS national databases. The results from these comparisons can be used to alert participating laboratories of possible deficiencies in their analytical operations. This program assigns an overall score from the results that a lab provides, and it also provides an individual rating for each analyte that is submitted and compared to the overall most probable number. The highest possible overall rating is 4.0 indicating excellent results, to a 0 for unsatisfactory results.

Our overall score for 2002, was 2.1, which was between satisfactory and good on the USGS rating score. Although this rating was lower than last year's number, we feel that we obtained very good results throughout the year.

Table 3-6. Individual scores for each analyte submitted to the USGS analytical evaluation program. All concentration data given in ppm, and conductivity given in $\mu\text{S}/\text{cm}$.

Analyte	pH	Conductance	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
MPV ¹	3.66	193	2.07	29.3	6.19	1.57	0.812	8.65
UT-results	3.65	200.7	1.84	30.53	7.92	1.57	0.74	8.12
Overall rating ²	4	3	0	3	0	4	1	2

1. Most probable values in the overall results.
2. Overall rating: 4 = excellent, 3 = good, 2 = satisfactory, 1.0 = marginal, and 0 = unsatisfactory.

The individual scores for each analyte are reported in Table 3-6. We scored excellent and good results for pH, conductivity, sulfate, and potassium. We did however receive unsatisfactory results for chloride and sodium, but these ratings are based on the overall Z-score of the program and we feel that we came rather close to the most probable values, considering that the sample was an unusual one for us. This particular unknown sample sent by the USGS for analysis was considerable higher than our highest standards for several measurements and had to be diluted for several analysis. Dilution of a sample can add another level of uncertainty to some measurements. We have done very well in the past with some of the analytes we did not perform as well this time, and believe we have accomplished acceptable results with our regular samples based on other QA/QC results.

3.5 Data Completeness

There are several types of data including stream survey and NDW grab samples; NDW continuous monitors for pH, conductivity, and flow; the open site and throughfall collectors; and lysimeters.

Estimating the amount of completeness for the deposition monitoring stations must consider that samples are combinations of multiple rain events collected since the last visit to the site. Since these samples are unprotected they are vulnerable to animal interaction. In 2002, we lost one collection from the throughfall site because of bear damage. An estimated or calculated value was given for the missing collection and added to the annual total amounts. From this adjusted total, a percentage of the actual total volumes collected can be calculated (Table 3-7).

Table 3-7. Wet-only and throughfall measurements and estimates for annual precipitation amounts entering the NDW in 2002.

	Wet-only precipitation	Throughfall
Missing volume ¹ , cm	0	4.23
Annual amount collected, cm	216.16	245.17
Estimated total annual amount, cm	216.16	249.40
Percentage of the estimated total that was collected	100%	98.3%

¹Missing volume estimates assume equal precipitation amounts between the adjacent throughfall and precipitation stations. If both stations were affected, then precipitation volume was taken from the weather station data set.

The continuous monitoring of stream pH and conductivity was interrupted on occasion due to either clogging of flow through sampling vessel port, loss of battery power, snow that dislodged electrical connections, and malfunctioning units. We estimate that 90% of the continuous stream pH and conductivity was captured. Stream flow measurements are interrupted on occasion due to freezing of the flumes' stilling wells. We estimate that better than 97% of the 15-minute stream flow data were captured.

NDW lysimeter samples are collected except when the sample collection system freezes or animal interaction occurs.

Stream survey and NDW samples are collected except in the rare occasion when the sites are inaccessible (e.g., Round-bottom road occasionally has many fallen trees across the road) or the streams are dry. We estimate that over 95% of all analyses were obtained. It is very rare that a sample analysis fails due to spilled samples or other reasons.

Appendix A-1

Aluminum Analysis Assessment Report

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Report Prepared for The National Park Service

October 31, 2002

EXECUTIVE SUMMARY

Alternative methods were investigated for analyzing aluminum in stream samples from the Great Smoky Mountains National Park. The aluminum analytical methods investigated by the previous and current researchers include a Skalar Auto-Analyzer, both flame and graphite furnace atomic absorption spectrophotometer methods, Hach eriochrome cyanine r method using a spectrophotometer, inductively coupled plasma (ICP) performed by the USGS, and samples analyzed by a private laboratory. These methods are briefly discussed below:

- **Skalar Auto-Analyzer:** In the early years of the project a Skalar Auto-Analyzer was used to measure Al in stream samples. However, after many attempts, the previous investigators concluded that the method could not produce accurate results and the analyses were halted shortly thereafter.
- **Flame Atomic Absorption Spectrophotometer:** At the low concentrations of Park samples the absorbencies were too low to provide a good quality fit for a standard curve.
- **Graphite Furnace Atomic Absorption Spectrophotometer:** Another AA method uses a graphite furnace to measure aluminum. To run this method, every sample would have had to be diluted because of the very narrow dynamic range of the instrument; thus sample preparation would very labor intensive. Also, working at such a low concentration range, contamination could be problematic. It was estimated that to do 25% of the current samples by graphite furnace would require on the order of two additional man-weeks per year plus supplies.
- **Hach Eriochrome Cyanine r Method using a Spectrophotometer:** This method worked well with Park samples, but it is not practical to run a large number of samples because sample preparation was very labor intensive. This method would require roughly two additional man-weeks per year plus reagents.

- Inductively Coupled Plasma: An ICP is an accepted method for analyzing low concentrations of aluminum in water samples. It is accurate and relatively fast and has a large dynamic range. Unfortunately, an ICP is not available to the project.
- Test America Private Laboratory: A selected number of samples from the August 2002 stream survey were sent to Test America, a private laboratory in Nashville, for aluminum analysis. The cost for sample analysis by Test America were \$11/sample.

Based on evaluating each of the methods above, it is our recommendation to send a select number of samples each year to a contract laboratory for aluminum analysis, such as Test America, until such time that an ICP or other suitable instrument can be procured. Approximately 15 samples from each quarterly stream survey would be sent per year, plus monthly samples from one of the streams at Noland Divide and the monthly lysimeter samples. Including about 10% QA/QC samples, this would be roughly 100 samples per year and would cost the project approximately \$1,200/yr. Based on earlier results it would not be necessary to run every sample collected. Samples to be sent for analysis would be chosen based on the historical chemistry data from that site, whether that site is a co-located fish study site, and current pH measurements from that sample. For example, if a sample came in with a relatively low pH for that period it would sent off for analysis. To prevent spurious aluminum results from particulates and sediments, samples will require filtering which would require roughly one to two days of hourly worker's time.

Appendix A-2

Water Quality and BMP Monitoring Report for Tunnel Reconstruction in the Great Smoky Mountains National Park

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Report Prepared for The National Park Service

December, 2002

EXECUTIVE SUMMARY

The University of Tennessee (UT) Civil and Environmental Engineering Department monitored the impact of road and tunnel reconstruction on adjacent streams in the Great Smoky Mountains National Park (GSMNP). The potential stream impacts of concern were sediment and acid generating geology. Sediment can adversely affect aquatic life and ecosystems by mechanical abrasion, obstructive silting, reducing the penetration of light, providing a surface for the growth of microorganisms, absorbing or adsorbing chemicals, and inhibiting normal temperature fluctuations (Swerdon and Kountz, 1973). Anakeesta exposure can upset aquatic life through depression of stream water pH and increased concentrations of toxic mineral elements, e.g., aluminum. This project also monitored Best Management Practice (BMP) performance for controlling erosion and sediment during reconstruction. BMPs were monitored because little information was available on the performance of these structures and efficiency results help in evaluating each structure's usefulness.

Monitoring took place on a reconstruction project 1.13 km (0.70 mi) in length on US 441 and included two tunnels through Chimney Tops Mountain and Morton Mountain. Reconstruction tasks included repairing the tunnels (deepening the tunnels, installing rock bolts, placing concrete tunnel sidewalls), roadway excavation, grading, drainage, new road base and paving, constructing guard walls, and other work. This report summarizes the pre-, during and post-construction monitoring from May 2001 through September 2002.

During pre- and post-construction periods, grab samples from Walker Camp Prong and the West Prong of the Little Pigeon River (WPLPR) were collected every two weeks at each of four stations: upstream and downstream of the two tunnel reconstruction sites. A passive sampling device was also located at each of the four stations, taking samples at various stage heights during high flows. During construction more frequent sampling occurred at these stations and around BMPs. The BMPs monitored were rock check dams, inlet protection for existing storm drains and disposal areas encapsulating spoil material. The rock check dams and inlet protection were installed to reduce suspended solids totals (by ponding water and allowing heavier particles to settle out). The check dams also reduced erosion by lowering the water's velocity and dissipating energy.

The tunnel reconstruction had no statistically identifiable impact on stream water quality. This conclusion is based on the following:

- Comparisons for upstream vs. downstream passive samples did not indicate that construction altered the pH or suspended solids concentration of the stream except that the Morton Tunnel sites showed higher pH downstream.
- Median suspended solids concentrations for the stream sampling locations were lower during construction than in the pre- and post-construction periods. The low suspended solids totals during construction (during winter) are likely because the ground was frozen during much of this period.
- Stream pH was lower during the construction period than the pre- and post-construction periods. However, paired differences (downstream value less the upstream value for each collection date) were examined to see if these pH trends were a result of seasonal variation. Other streams within the same watershed did show pH differences consistent with the variation observed at the Morton sites (indicating seasonality).
- For each tunnel the water quality parameters that varied between the upstream and downstream sampling during the construction periods were the same ones that varied prior to construction.
- The area of disturbance was small compared to the watershed. Approximate calculations showed that little impact should be expected because the storm runoff volume from the construction site was very small in comparison to the stream flow from the watershed.

BMP performance varied. Success or failure was tied to proper/improper location, design, construction and maintenance. Specific conclusions include:

- Many BMPs were installed according to the plans but were not constructed in locations where they would receive runoff from construction activities.
- Multiple BMPs were added and/or altered after construction began as unforeseen or newly developed runoff conditions were discovered.
- The efficiency of check dams was dependent upon their ability to pond water and the pond volume available for ponding and storage. The rock check dam at the Old Trace Road Disposal site provided area for storage and offered good settleable solids trapping efficiency for runoff events with high suspended solids concentrations (90% and 65% removals for influents of 23,567 and 42,527 mg/L respectively). The rock check dams installed at the Chimneys site provided very little ponding and therefore negligible trapping efficiency. A statistically significant difference was not detected in the suspended solids concentrations before and after Chimney Tops rock check dams ($p=0.813$) and inlet protection at Morton Mountain ($p=0.195$). Despite these findings field observance did reveal trapped sediment behind rock check dams indicating that some material was retained by the structures.

- A statistically significant difference was not detected in the pH above and below the rock check dams and inlet protection at Chimney Tops ($p=0.813$) and Morton Mountain ($p=0.250$).
- Silt fences were not observed ponding water at any location.
- The disposal practices used for the excavated materials were effective in neutralizing any acidic leachate. The pH of leachate from the disposal mound at Old Trace Road ranged from 6.9 to 7.7. Gnatty Branch disposal mound leachate pH measured 7.2 or greater.

Information in addition to construction impact or BMP performance was gained from this project:

- Storm runoff lowered stream pH values. The effect was more pronounced at the Morton locations. Median pH at the uppermost stream sampling station decreased by 1.1, 0.7 and 0.9 units for the three monitoring periods respectively when comparing baseflow samples with the highest stage passive collection bottle. Likewise, the Morton sites experienced greater changes during storm events than the Chimney's sites for other water quality parameters.
- Higher flows also resulted in higher suspended solids concentrations. Median concentrations were at least three-fold greater for the highest stage passive collection bottles than for the lowest stage (for all but one out of twelve cases).
- Regular inspection and maintenance is required for BMPs to function properly.
- Excavated material was tracked onto the haul road and contaminated runoff during rain events. Much of this material could have been recovered if a street sweeping truck had been used.

