

Smoky Mountains Water Quality Annual Report for 2003

R. Bruce Robinson, Ph.D., P.E.
Professor of Civil and Environmental Engineering

John Shubzda
Research Associate

Thomas Barnett
Graduate Research Assistant

Department of Civil and Environmental Engineering
The University of Tennessee
Knoxville, TN 37996
(865) 974-7730

April 22, 2004

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

TABLE OF CONTENTS

	Page
1. Noland Divide Watershed	1
1.1 Annual Deposition Rates	1
1.2 Soil Lysimeter Chemistry	5
2. Stream Survey Results	7
3. Overall QA/QC Procedures	13
3.1 Ion Chromatography QA/QC Procedures	15
3.2 Atomic Absorption QA/QC Procedures	19
3.3 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) QA/QC Procedures	23
3.4 Ion Balance	25
3.5 Data Completeness	26
4. References	29

List of Tables

Table 1-1. Statistical summaries for pH and conductivity from the soil lysimeters	5
Table 1-2. Statistical summaries of the anion chemistry analysis on the soil lysimeter samples	5
Table 1-3. Statistical summaries of the cation chemistry analysis on the soil lysimeter samples	6
Table 2-1. Descriptive statistics of 1993-2002 median water quality values for all sites	8
Table 2-2. Descriptive statistics of 2003 median water quality values for all sites	8
Table 2-3. pH effects and the percentage of sampling sites with median pH within the range	9
Table 3-1. Analytical procedures for chemistry analysis preformed at the University of Tennessee	14
Table 3-2. QA\QC results of the IC analysis for selected anions	16
Table 3-3. QA\QC results of the IC analysis for monovalent cations	16
Table 3-4. Average QA\QC results of the AA analysis for magnesium and calcium	20
Table 3-5. ICP results for the prepared quality assurance sample	23
Table 3-6. ICP results for the USGS trace metal sample	24
Table 3-7. ICP results for blanks	24
Table 3-8. ICP results for replicates	25
Table 3-9. Average ion balances for both streamlets, precipitation and throughfall	26
Table 3-10. Wet-only and throughfall measurements and estimates for annual precipitation amounts entering the NDW in 2003	27

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 2-1. Scatter plot of median pH values versus elevation	10
Figure 2-2. Scatter plot of median ANC values versus elevation	11
Figure 3-1. Chloride concentrations made on laboratory check sample over multiple runs	17
Figure 3-2. Sodium concentrations made on laboratory check sample over multiple runs	18
Figure 3-3. Magnesium standard check sample results plotted over the course of the analysis	21
Figure 3-4. Calcium standard check sample results plotted over the course of the analysis	22

This report describes calendar year (CY) 2003 work accomplished under Amendment No. 7 to Cooperative Agreement No. **1443-CA-5460-98-007** 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 2003, the estimated amount of total inorganic nitrogen entering the Noland Divide Watershed (NDW) as throughfall was 1228 equivalents of nitrogen per hectare per year (eq/ha/yr), and 522 (eq/ha/yr) was collected as wet-only precipitation (see Figure 1-1). These deposition rates were very close to the 11 year average deposition rates recorded since the project began in 1991.

The estimated amount of sulfate entering the NDW as throughfall was 1528 (eq/ha/yr), and 440 (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 2003 was 207 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 (Lovet and Kinsman, 1991).

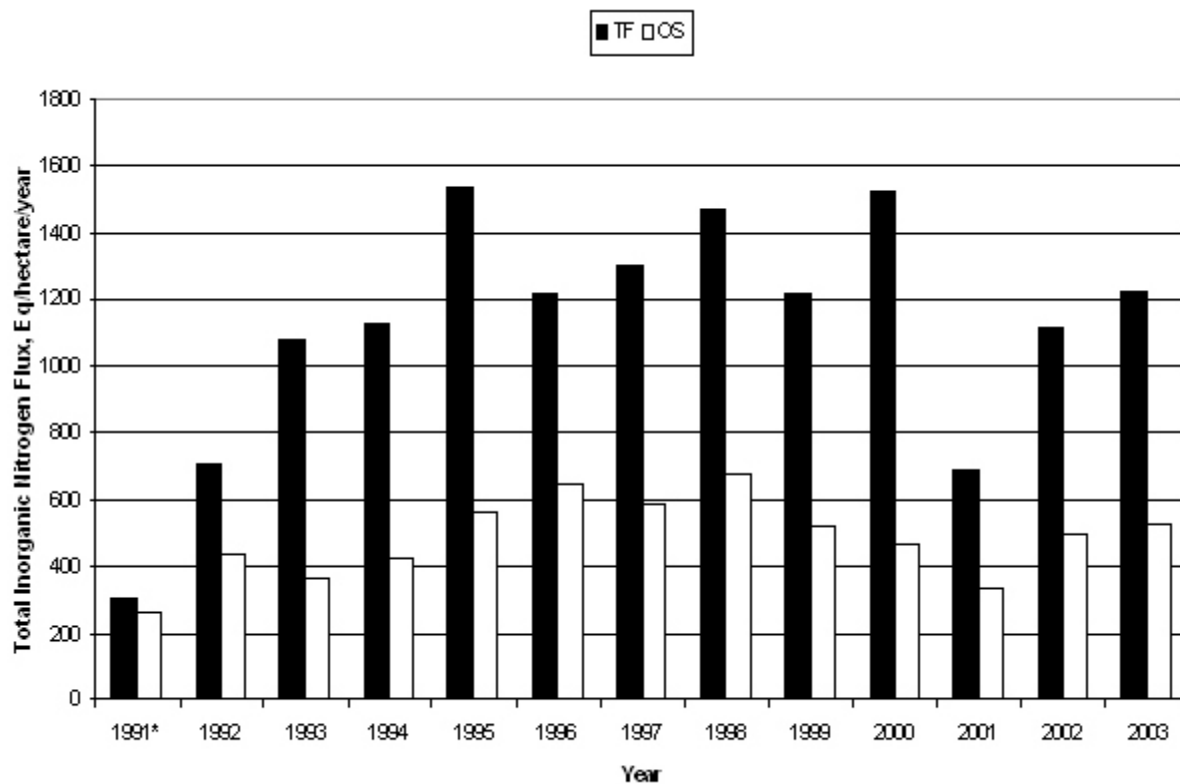


Figure 1-1. Total inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation. *The collections in 1991 started in June, and represent only half of the years total deposition rates.

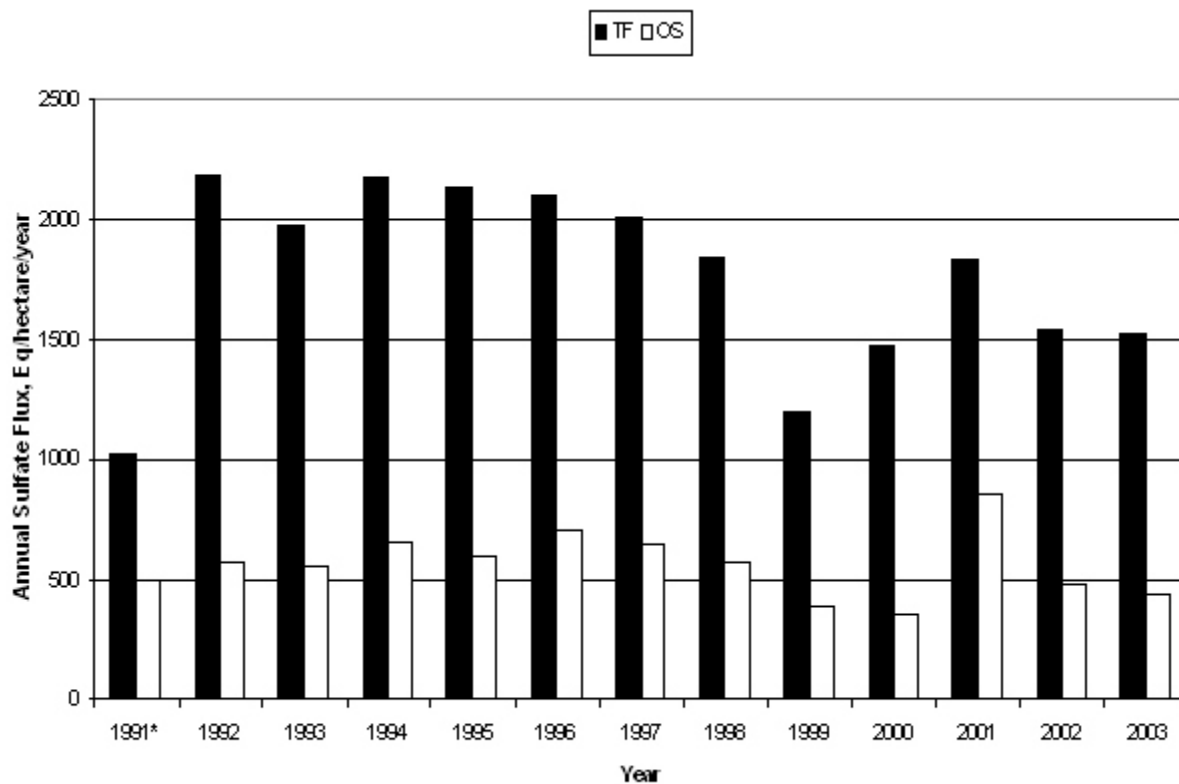


Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation. *The collections in 1991 started in June, and represent only half of the years total deposition rates.

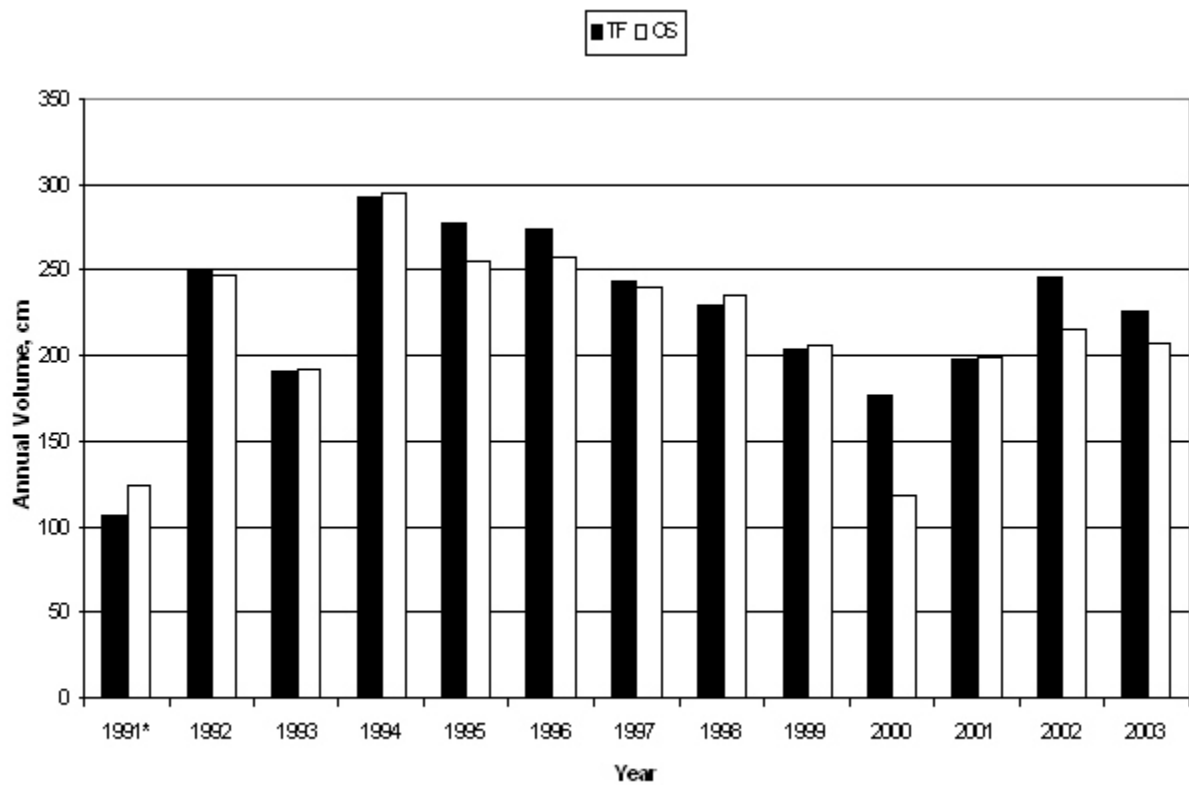


Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW. *The collections in 1991 started in June, and represent only half of the total deposition rates.

1.2 Soil Lysimeter Chemistry

Soil water chemistry is collected monthly from 12 lysimeters located at 3 different depths within NDW. The annual volumes for the upper, middle, and lower lysimeters were 3580, 4257, and 9784 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, S/cm ²
Upper Lysimeter	Minimum	3.36	26.90
	Average	4.07	62.64
	Maximum	4.53	158.50
Middle Lysimeter	Minimum	4.13	27.80
	Average	4.31	35.90
	Maximum	4.54	52.50
Lower Lysimeter	Minimum	4.11	28.30
	Average	4.44	31.87
	Maximum	4.59	37.10

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

		Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Upper Lysimeter	Minimum	12.56	35.45	58.68
	Average	21.41	156.45	76.06
	Maximum	42.67	520.52	136.66
Middle Lysimeter	Minimum	16.39	25.75	56.26
	Average	29.35	65.30	76.23
	Maximum	46.31	105.81	85.57
Lower Lysimeter	Minimum	14.13	40.20	68.09
	Average	20.54	71.34	74.75
	Maximum	39.80	100.22	79.79

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

		Na⁺	K⁺	Mg²⁺	Ca²⁺
Upper Lysimeter	Minimum	14.05	1.14	17.94	24.80
	Average	23.30	6.34	27.12	49.67
	Maximum	40.94	14.68	51.75	81.85
Middle Lysimeter	Minimum	22.46	3.46	17.70	22.94
	Average	25.59	6.58	20.73	30.88
	Maximum	28.14	14.12	25.43	37.97
Lower Lysimeter	Minimum	13.38	4.55	20.07	30
	Average	20.33	6.03	22.84	37.62
	Maximum	25.97	8.09	28.18	46.09

2.0 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, 2003. Throughout the following text, comparisons will be made between the data collected in 2003 and previous data collected from October, 1993 to November, 2002.

Table 2-1 shows descriptive statistics of the water quality constituents for the 1993 to 2002 data set. The descriptive statistics are applied to the set of median water quality values for each sampling site. Table 2-2 gives the descriptive statistics of the median water quality values for the 2003 data. The descriptive statistics for the two data sets are quite similar.

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 2-3 lists several pH ranges, potential biological effects, and the percentage of sample sites with median pH within those ranges for the 2003 and 1993-2002 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 2003 data changes slightly from the 1993-2002 data set. The 2003 data has four more sites with median pH values in the 6 to 8 range where there are little to no effects on trout species.

Figure 2-1 is a scatter plot of median pH values for the 2003 and 1993-2002 data plotted by elevation. Figure 2-2 is a scatter plot of median ANC values for the 2003 and 1993-2002 data plotted by elevation. The plots show that overall median pH and ANC values decrease with increasing elevation.

Table 2-1. Descriptive statistics of 1993-2002 median water quality values for all sites

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation
Median pH	4.820	7.430	6.219	0.496
Median ANC (meq/L)	-14.360	1043.911	80.141	179.720
Median Conductivity (mS/cm)	7.555	96.300	18.089	15.158
Median Chloride (meq/L)	11.868	22.452	15.226	1.983
Median Nitrate (meq/L)	0.000	78.635	21.161	17.757
Median Sulfate (meq/L)	8.234	286.034	43.532	44.149
Median Sodium (meq/L)	17.842	69.628	36.627	10.074
Median Ammonium (meq/L)	0.000	0.000	0.000	0.000
Median Potassium (meq/L)	3.233	16.180	10.141	2.927
Median Magnesium (meq/L)	9.465	199.794	33.420	32.181
Median Calcium (meq/L)	17.375	773.000	79.909	132.495

Table 2-2. Descriptive statistics of 2003 median water quality values for all sites

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation
Median pH	4.751	7.728	6.477	0.583
Median ANC (eq/L)	-16.526	979.050	80.060	159.763
Median Conductivity (S/cm)	7.735	100.900	18.229	15.068
Median Chloride (eq/L)	13.801	27.743	19.532	3.599
Median Nitrate (eq/L)	0.000	74.151	19.370	16.591
Median Sulfate (eq/L)	7.471	164.993	38.577	28.973
Median Sodium (eq/L)	18.541	68.797	39.636	9.508
Median Ammonium (eq/L)	0.000	4.280	0.189	0.811
Median Potassium (eq/L)	5.303	17.055	10.553	2.671
Median Magnesium (eq/L)	10.305	184.321	33.822	29.447
Median Calcium (eq/L)	28.250	698.977	79.437	111.976
Median Aluminum (ppm)	0.000	0.120	0.028	0.027
Median Copper (ppm)	0.000	0.011	0.001	0.002
Median Iron (ppm)	0.000	0.061	0.008	0.013
Median Manganese (ppm)	0.000	0.058	0.002	0.009
Median Silicon (ppm)	0.000	3.591	0.911	0.731
Median Zinc (ppm)	0.000	0.060	0.009	0.010

Table 2-3. pH effects and the percentage of sampling sites with median pH within the range

pH Range	Effects	% Sampling Sites 10/93 to 11/02	% Sampling Sites 3/03 to 11/03
8.0-6.0	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%	75/90 = 83.3%
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%	14/90 = 15.5%
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%

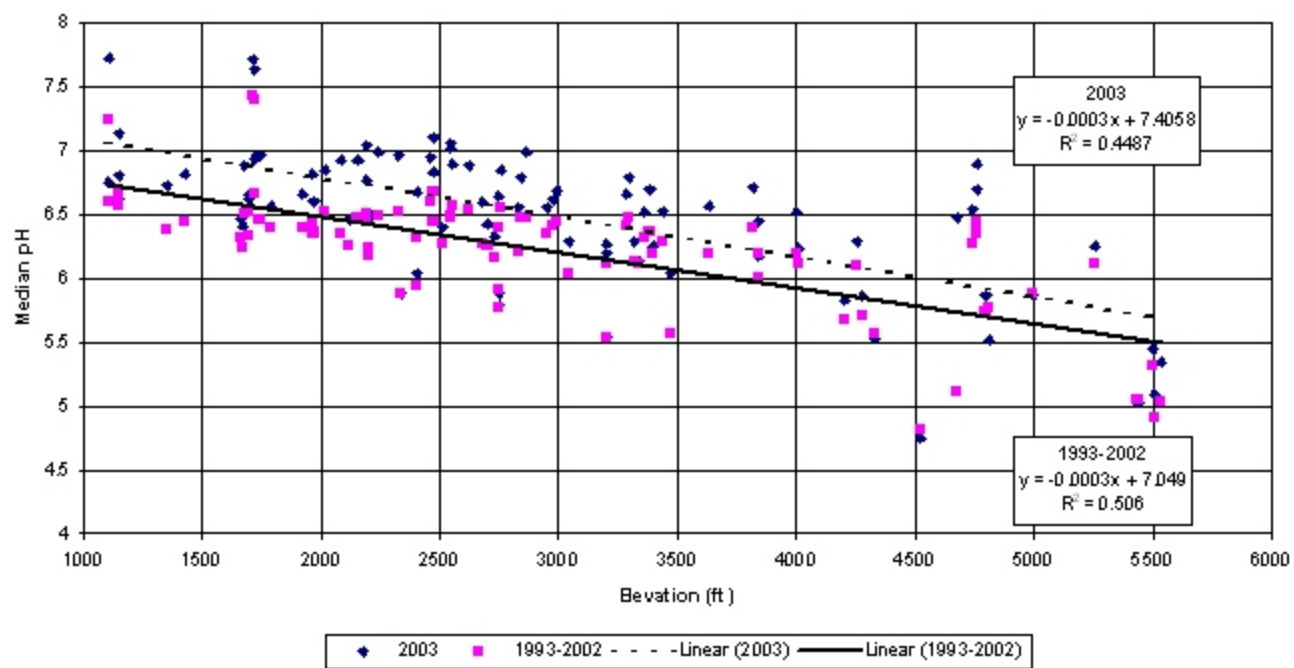


Figure 2-1. Scatter plot of median pH values versus elevation

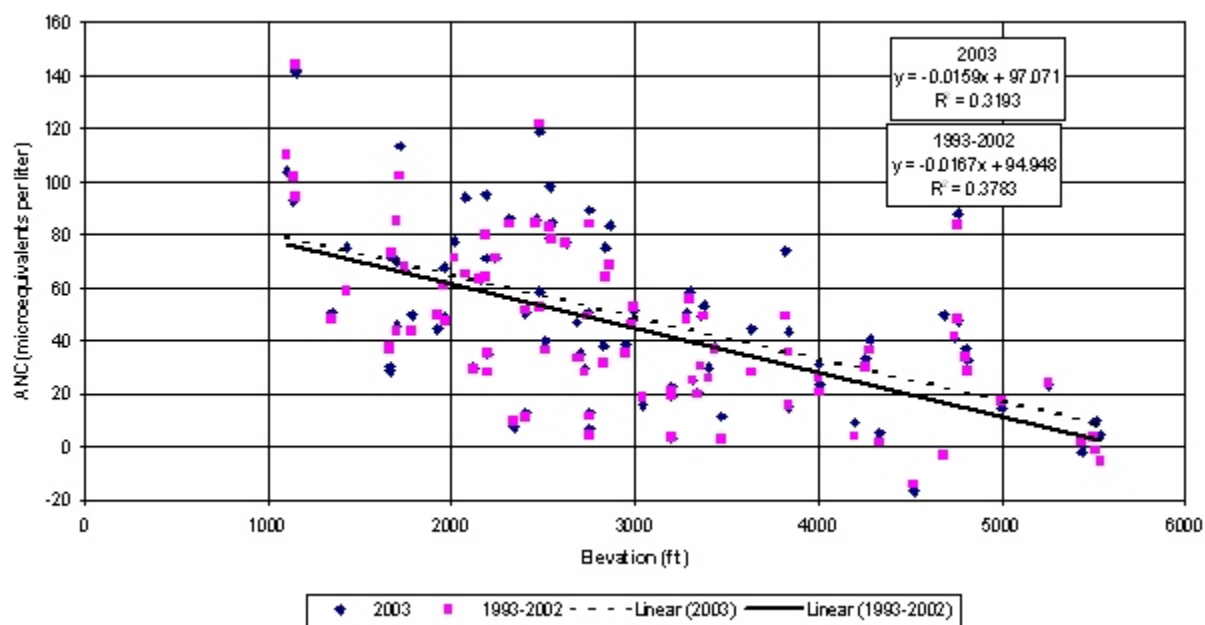


Figure 2-2. Scatter plot of median ANC values versus elevation

Starting with the August survey, trace metals were analyzed using an ICP. Of the 165 samples analyzed, 45 had aluminum values between 100 and 200 ppb and 6 had values greater than 200 ppb. A threshold in the 100 to 200 ppb range seems to be where the negative effects of aluminum on trout begin and increase with increasing aluminum concentrations. However, the negative effects of Al on trout are also dependent upon pH and other ionic concentrations (Ca, Na, K, etc). For copper, 41 of 146 samples exceeded EPA's criterion continuous concentration (CCC) of 9.0 µg/L and 24 of 146 samples exceeded the criterion maximum concentration (CMC) of 13 µg/L (USEPA 2002). The CCC and CMC are for a hardness level of 100 mg/L and have not been adjusted for the much lower hardness in GRSM waters. It is not clear that the EPA hardness adjustment formulas were intended for low conductivity waters. If the EPA formulas were applied, the CCC and CMC are less than 1 µg/L. Similarly, 7 of 146 samples exceeded the CCC and CMC both of which are 120 µg/L.

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	Radiometer Auto-titrator	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
Earth and Trace Metals (Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Mn ²⁺ , Al ³⁺ , Fe ³⁺ , Cu ²⁺ , Zn ²⁺ , & Si)	Inductively Coupled Plasma Spectrometer	Thermo- Elemental	Standard Methods 3120B EPA Method 6010B EPA Method 3005A

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 S/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 chloride measurements during several different runs. Figure 3-2 shows multiple sodium 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	0.995	0.996	0.994
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	2.20% (n=13)	1.82% (n=13)	0.47% (n=13)

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	0.993	0.995	0.992
Acidification blanks	not detected	not detected	not detected
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	0.71% (n=13)	0% (n=5)	0.28% (n=13)

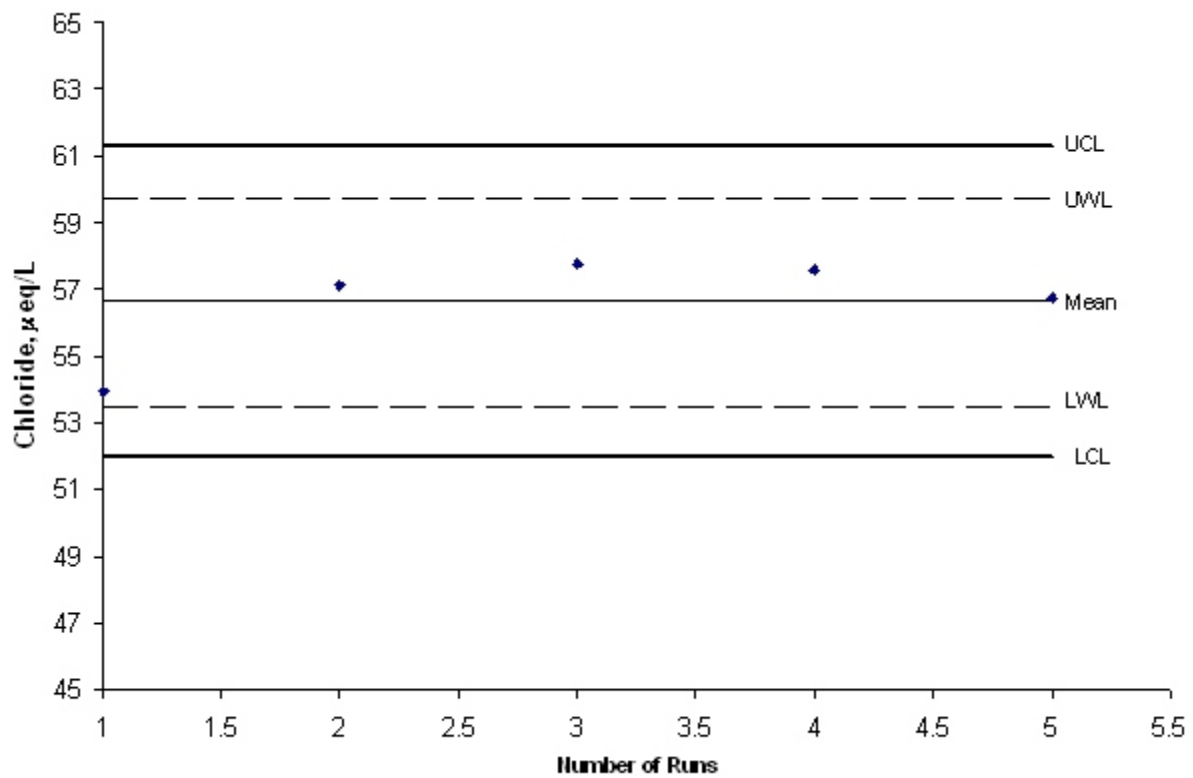


Figure 3-1. Chloride concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (± 3 S.D.); UWL and LWL = upper and lower warning limits (± 2 S.D.).

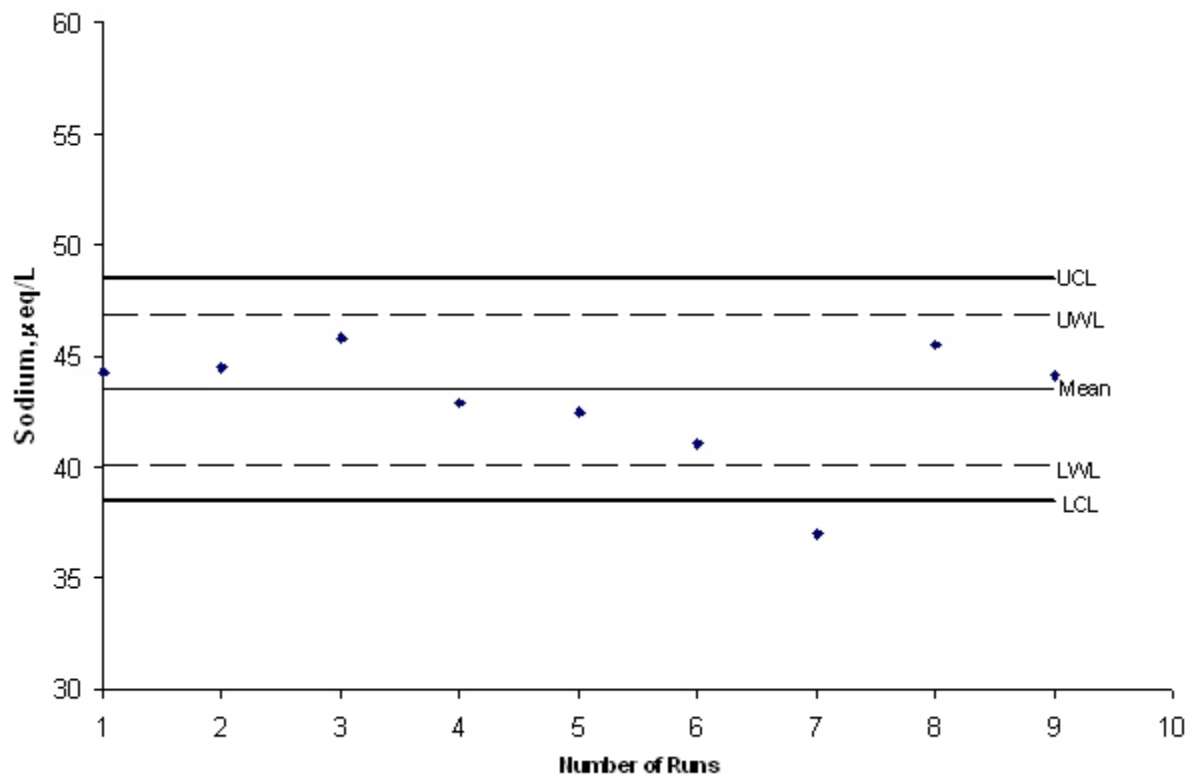


Figure 3-2. Sodium concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (± 3 S.D.); UWL and LWL = upper and lower warning limits (± 2 S.D.).

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	100.33% (n=2)	111.94% (n=3)

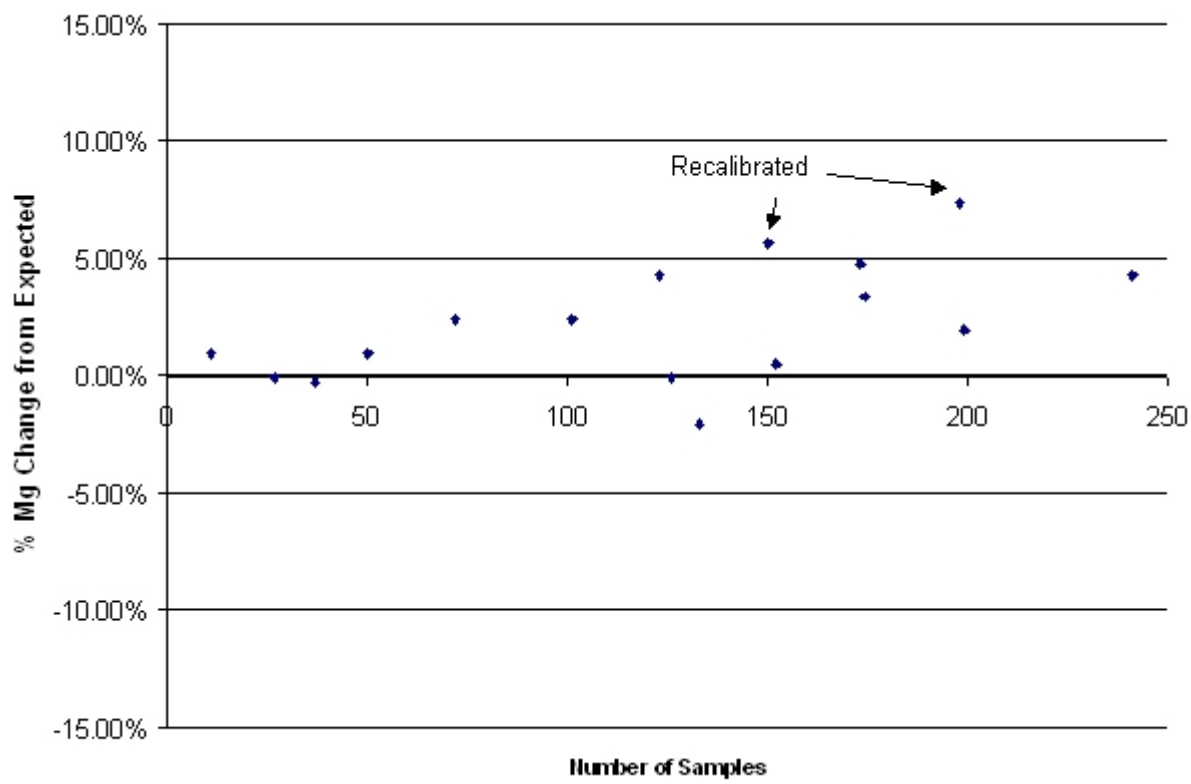


Figure 3-3. Magnesium standard check sample results plotted over the course of the analysis.

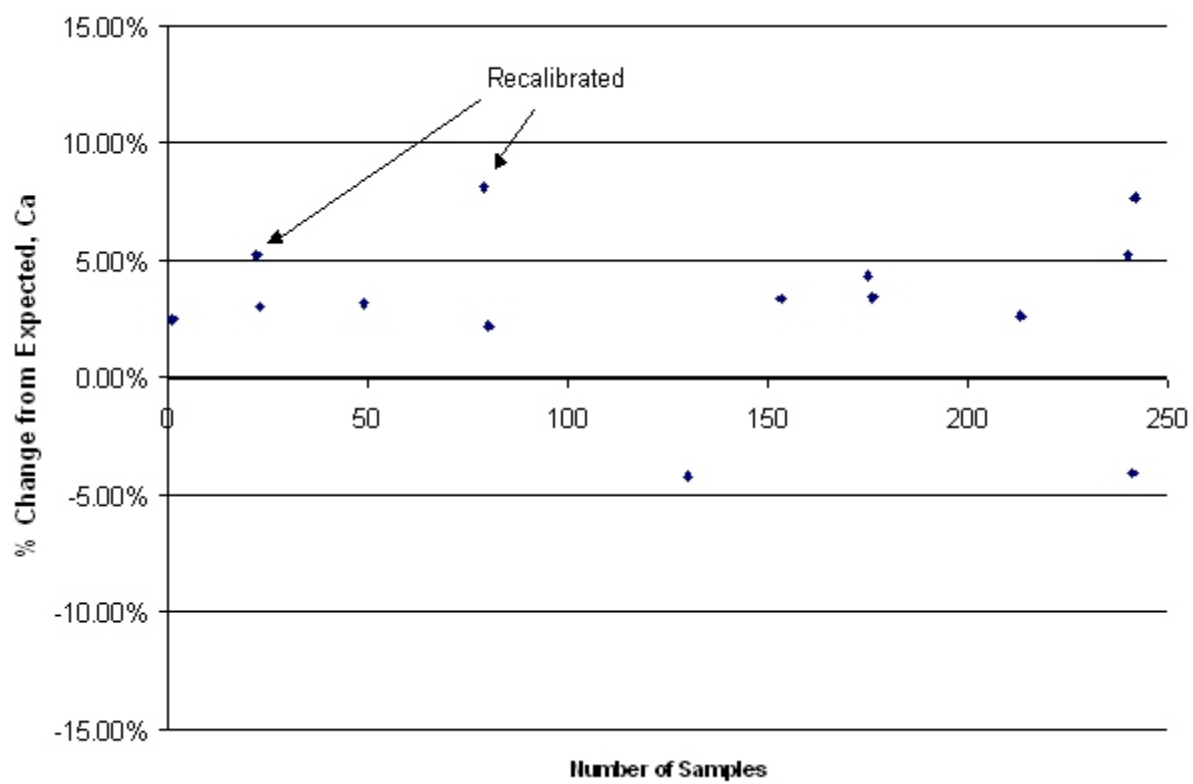


Figure 3-4. Calcium standard check sample results plotted over the course of the analysis.

3.3 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) QA/QC Procedures

The ICP is used to analyze major cations (Na, K, Mg, Ca) and six trace metals (Al, Cu, Fe, Mn, Si, Zn). Several QA/QC procedures are performed to ensure attainment of the highest quality data. About 348 field samples and 68 QA/QC samples (about 20 percent) have been analyzed on the ICP. Standards are prepared using certified ICP reagents and deionized water. The standard curves produced by the instrument are checked to insure linearity ($R^2 > 0.999$) prior to sample introduction. A QA sample is also prepared from the certified reagents and DI and ran every 12 to 15 samples to ensure accuracy throughout the run. The results for the QA samples are presented in table 3-5. Average percent errors are less than 3% for each element.

Table 3-5. ICP results for the prepared quality assurance sample

Element	Mean Value (ppm)	#	Std. Deviation	Actual Value (ppm)	% ERROR
Aluminum	0.505	31	0.015	0.5	1.02
Calcium	2.043	31	0.051	2.0	2.14
Copper	0.493	31	0.012	0.5	1.35
Iron	0.997	31	0.027	1.0	0.32
Potassium	0.982	31	0.101	1.0	1.83
Magnesium	2.058	31	0.054	2.0	2.92
Manganese	0.502	31	0.010	0.5	0.34
Sodium	1.027	31	0.016	1.0	2.73
Silicon	1.015	31	0.041	1.0	1.51
Zinc	0.512	31	0.019	0.5	2.42

A USGS trace metal sample was purchased and ran every 20 samples. The most probable

values were obtained from the USGS and compared to results from the ICP. The results are presented in table 3-6. The percent errors obtained are good with the exceptions of iron, copper, and aluminum which are fair. The actual concentrations of Al, Fe, and Cu are in the low parts per billion and even small variations can cause significant errors.

Table 3-6. ICP results for the USGS trace metal sample

Element	Mean Value (ppm)	#	Std. Deviation	Actual Value (ppm)	% ERROR
Aluminum	0.084	19	0.019	0.071	18.61
Calcium	34.864	19	0.919	34.800	0.18
Copper	0.0084	19	0.007	0.0075	12.42
Iron	0.025	19	0.007	0.021	17.90
Potassium	3.908	19	0.240	3.850	1.50
Magnesium	9.202	19	0.282	9.380	1.89
Manganese	0.482	19	0.015	0.495	2.69
Sodium	34.349	19	1.461	36.500	5.89
Silicon	5.175	19	0.218	5.180	0.09
Zinc	0.340	19	0.017	0.348	2.29

Field and reagent blanks were made and ran and the results are presented in table 3-7. Most of the values are in the very low parts per billion.

Table 3-7. ICP results for blanks

Element	Mean Value (ppm)	#
Aluminum	0.026	10
Calcium	0.182	10
Copper	0.004	10
Iron	0.038	10
Potassium	0.141	10
Magnesium	0.030	10
Manganese	0.002	10
Sodium	0.170	10
Silicon	0.065	10
Zinc	0.039	10

Sample replicates were also prepared and ran. The results are presented in table 3-8. The percent differences are fairly low except for copper and zinc which had very low concentrations (<10 ppb) which can cause large percent errors for small variations in concentration.

Table 3-8. ICP results for replicates

Element	Average Absolute Percent Difference	#
Aluminum	6.54	8
Calcium	4.83	8
Copper	24.54	8
Iron	14.29	8
Potassium	5.16	8
Magnesium	10.60	8
Manganese	4.62	8
Sodium	2.71	8
Silicon	14.21	8
Zinc	24.51	8

3.4 Ion Balance

Once 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 3-9 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 3-9. Average ion balances for both streamlets, precipitation and throughfall.

	NE Streamlet	SW Streamlet	Open Site	Throughfall
% Ion balance	-7.38%	-7.49%	-0.40%	-0.08%

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 2003, we lost two collections from the throughfall and open site because of bear damage, and two collections at the open site due to Aero-chem malfunction. 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 3-10).

Table 3-10. Wet-only and throughfall measurements and estimates for annual precipitation amounts entering the NDW in 2003.

	Wet-only precipitation	Throughfall
Missing volume ¹ , cm	32.47	8.52
Annual amount collected, cm	207.22	225.46
Estimated total annual amount, cm	239.69	233.98
Percentage estimated relative to total volume	13.54%	3.64%

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 25% of the continuous stream pH and 75 % of the conductivity and temperature was captured. Stream flow measurements are interrupted on occasion due to freezing of the flumes' stilling wells. We estimate that better than 98% 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. Usually over 95% of all samples are obtained. However, spring floods damaged many areas of the park and made roads inaccessible. Therefore, several stream survey routes were not collected due to logistics (most notably the Hazel creek route). There were 305 stream survey samples collected for 2003. This represents about 85 % of the total samples normally collected (360 total).

4.0 References

Garten, C.T., Bondietti, E.A., Lomax, R. D. 1988. Contribution of foliar leaching and dry deposition to sulfate in net throughfall below deciduous trees. *Atmospheric Environment* 22: 1425-1432.

Lindberg, S.E., and C.T. Garten. 1988. Sources of sulfur in forest canopy throughfall. *Nature* 336: 148-151.

Lovett, G.M., and J.D. Kinsman. 1991. Atmospheric pollutant deposition to high elevation ecosystems. *Atmospheric Environment* 24A: 2767-2786.

Shubzda, J., Lindberg, S.E., Garten, C.T., and Nodvin, S.C. 1995. Elevational trends in the fluxes of sulfur and nitrogen in throughfall in the Southern Appalachian Mountains: Some surprising results. *Water, Air, and Soil Pollution*. 85: 2265-2270.

U.S. Environmental Protection Agency. *National Recommended Water Quality Criteria: 2002*. EPA-822-R-02-047. Office of Science and Technology (4304T), November 2002.
<http://www.epa.gov/waterscience/pc/revcom.pdf>