Smoky Mountains Water Quality Annual Report for 2006

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This report describes for water quality monitoring in the Great Smoky Mountains National Park for calendar year (CY) 2006 work accomplished under Amendment No. 7 to Cooperative Agreement No. **1443-CA-5460-98-007** between the University of Tennessee and the National Park Service and also under the Southern Appalachian Cooperative Ecosystem Studies Unit CESU Host Cooperative Agreement No. H5000 04 5040 Task Agreement No. J5460 05 0067 between the National Park Service and the University of Tennessee

1.0 Noland Divide Watershed

1.1 Annual Deposition Rates

During the year 2006, the estimated amount of total inorganic nitrogen entering the Noland Divide Watershed (NDW) as throughfall was 1339.51 equivalents of nitrogen per hectare per year (eq/ha/yr), and 485.70 (eq/ha/yr) was collected as wet-only precipitation (see Figure 1-1). These deposition rates were slightly higher than last year's totals but very close to the 15 year average deposition rates recorded since the project began in 1991.

The estimated amount of sulfate entering the NDW as throughfall was 1992.09 (eq/ha/yr), and 634.10 (eq/ha/yr) as wet-only precipitation (Figure 1-2). These deposition rates were above the 15 year average deposition rates. 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 2006 was about 203 cm (Figure 1-3), while surrounding lowland areas such as Knoxville, TN generally average around 121.4 cm/yr (www.ncdc.noaa.gov, 2007). 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).

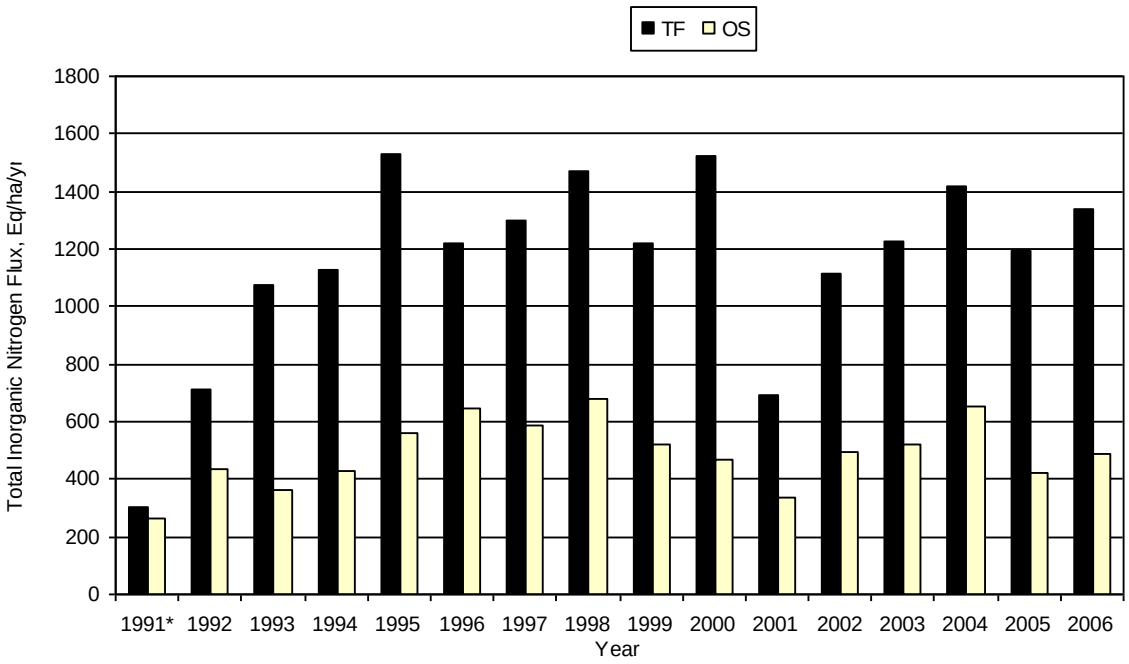


Figure 1-1. Total inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation.
*The collections in 1991 started in June, and represent only half of the years total deposition rates.

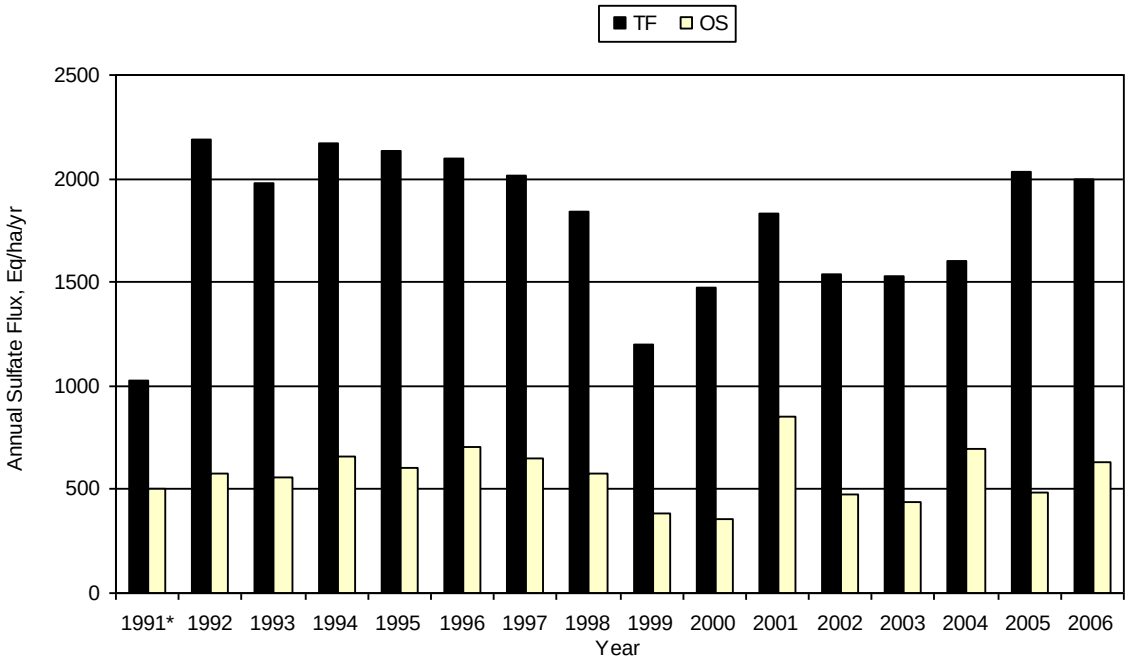


Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation.
*The collections in 1991 started in June, and represent only half of the years total deposition rates.

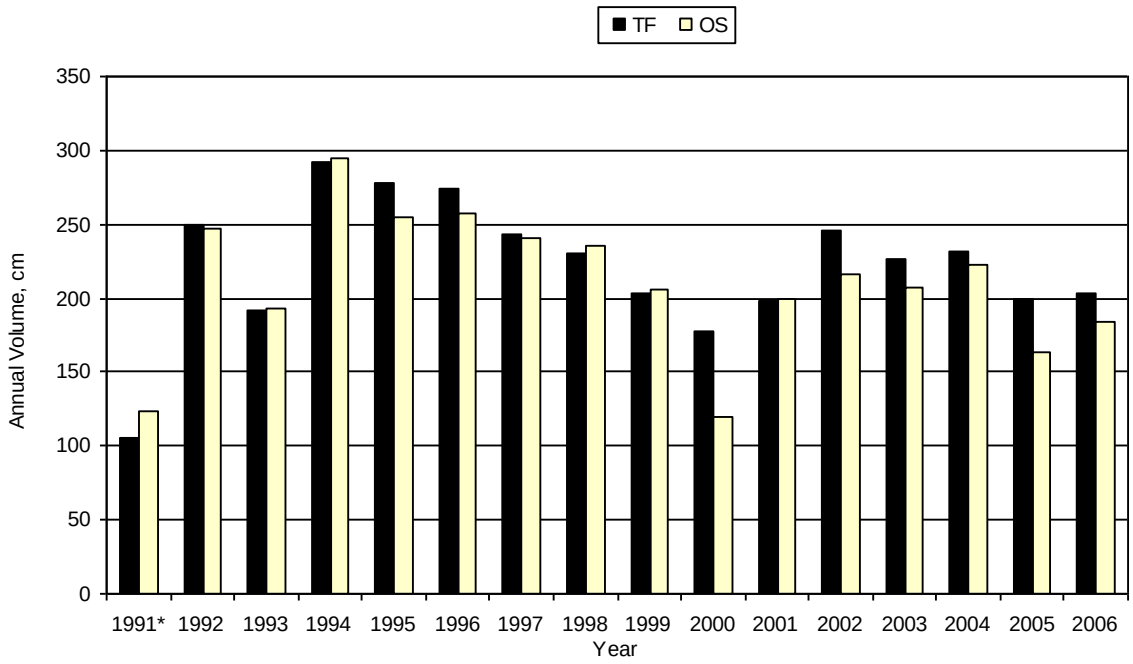


Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW. *The collections in 1991 started in June, and represent only half of the total deposition rates.

1.2 Soil Lysimeter Chemistry

Soil water chemistry is collected monthly from 12 lysimeters located at 3 different depths within the NDW. The annual volumes for the upper, middle, and lower lysimeters were 1240, 1220, and 5620 mL, respectively. Statistical summaries of the chemistry in soil 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, μS/cm^2
Upper Lysimeter	**Minimum**	**3.70**	**58.10**
	Average	**3.89**	**98.54**
	Maximum	**4.41**	**119.50**
Middle Lysimeter	**Minimum**	**3.55**	**42.50**
	Average	**4.00**	**82.62**
	Maximum	**4.38**	**152.90**
Lower Lysimeter	**Minimum**	**4.08**	**30.70**
	Average	**4.49**	**45.18**
	Maximum	**5.00**	**60.90**

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

		Cl^-	NO_3^-	SO_4^{2-}
Upper Lysimeter	**Minimum**	**23.48**	**202.61**	**79.90**
	Average	**31.41**	**225.25**	**113.59**
	Maximum	**42.86**	**239.90**	**141.05**
Middle Lysimeter	**Minimum**	**13.53**	**120.91**	**75.42**
	Average	**24.37**	**219.39**	**99.71**
	Maximum	**44.91**	**360.70**	**132.37**
Lower Lysimeter	**Minimum**	**16.48**	**90.67**	**70.70**
	Average	**20.25**	**160.79**	**81.07**
	Maximum	**25.90**	**203.11**	**94.34**

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

		Na^+	K^+	Mg^{2+}	Ca^{2+}
Upper Lysimeter	**Minimum**	**19.91**	**4.74**	**11.23**	**12.49**
	Average	**62.16**	**78.50**	**30.24**	**54.56**
	Maximum	**67.73**	**94.10**	**67.89**	**136.45**
Middle Lysimeter	**Minimum**	**17.32**	**7.40**	**25.38**	**18.79**
	Average	**55.68**	**25.92**	**27.46**	**33.89**
	Maximum	**84.03**	**42.45**	**33.85**	**46.27**
Lower Lysimeter	**Minimum**	**18.28**	**7.55**	**29.29**	**36.02**
	Average	**31.99**	**11.83**	**31.15**	**42.12**
	Maximum	**44.26**	**15.73**	**32.38**	**51.28**

2.0 Stream Survey Results

Stream survey within GRSM began from October 1993. Since then, total 92 sites have been investigated. In 2004, stream survey on some sites was stopped, and the number of survey sites was decreased from 90 to 43. In order to keep the consistency, only the survey results from the 43 remaining sites are discussed.

The data set includes samples collected from thirty-two sites during six stream surveys in January, March, May, July, September and November 2006 and eleven samples collected from the Hazel Creek watershed in March and September of 2006. Throughout the following text, comparisons will be made between the data collected in 2006 and previous data collected from October 1993 to November 2005.

Table 2-1 shows descriptive statistics of the water quality constituents for the 1993 to 2005 data set for the 43 sites (trace metals analyses to include Al, Cu, Fe, Mn, Si and Zn began in August 2003). 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 2006 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 2006 and 1993-2005 data sets, although the reader should understand that some of the low pH streams may be too small to support trout and that many other factors are also important for aquatic organisms. The percentages of sampling sites within each range for the 2006 data changes slightly from the 1993-2005 data set. The 2006 data has more acidic sites with median pH value below 6 where it is harmful to trout species.

Figure 2-1 is a scatter plot of median pH values for the 2006 and 1993-2005 data plotted by elevation.

Figure 2-2 is a scatter plot of median ANC values for the 2006 and 1993-2005 data plotted by elevation.

The plots show that overall median pH and ANC values decrease with increasing elevation. The decreasing tendency is similar for the 2006 and 1993-2005 data sets.

Table 2-1 Descriptive statistic of 1993-2005 median water quality values for 43 sites

Water Quality Parameter	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**
Median pH	4.810	7.430	6.363	0.436
Median ANC (μeq/L)	-14.360	964.507	98.681	181.637
Median Conductivity (μS/cm)	10.485	96.300	19.871	16.854
Median Chloride (μeq/L)	9.261	21.552	15.064	2.086
Median Nitrate (μeq/L)	0.000	56.793	18.216	16.078
Median Sulfate (μeq/L)	14.437	280.682	44.356	46.999
Median Sodium (μeq/L)	17.828	67.748	39.790	9.826
Median Ammonium (μeq/L)	0.000	0.000	0.000	0.000
Median Potassium (μeq/L)	3.550	16.128	10.656	2.828
Median Magnesium (μeq/L)	16.647	181.275	41.109	35.693
Median Calcium (μeq/L)	32.154	764.500	97.021	149.532
Median Aluminum (ppm)	0.019	0.363	0.052	0.057
Median Copper (ppm)	0.001	0.050	0.005	0.008
Median Iron (ppm)	0.010	0.041	0.023	0.008
Median Manganese (ppm)	0.008	0.564	0.126	0.147
Median Silicon (ppm)	1.339	4.510	2.740	0.629
Median Zinc (ppm)	0.004	0.181	0.017	0.027

Table 2-2. Descriptive statistics of 2006 median water quality values for 43 sites.

Water Quality Parameter	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**
Median pH	4.836	7.508	6.351	0.497
Median ANC (μeq/L)	-7.690	900.634	88.779	176.116
Median Conductivity (μS/cm)	10.810	100.350	21.440	18.565
Median Chloride (μeq/L)	9.303	17.930	12.022	1.821
Median Nitrate (μeq/L)	0.937	63.705	22.523	18.773
Median Sulfate (μeq/L)	16.047	396.213	48.754	60.554
Median Sodium (μeq/L)	21.718	57.026	36.959	8.880
Median Ammonium (μeq/L)	0.000	1.675	0.110	0.284
Median Potassium (μeq/L)	4.722	16.118	10.817	2.635
Median Magnesium (μeq/L)	15.969	172.945	42.728	36.874
Median Calcium (μeq/L)	30.893	770.668	94.348	146.220
Median Aluminum (ppm)	0.000	0.655	0.045	0.098
Median Copper (ppm)	0.000	0.059	0.002	0.009
Median Iron (ppm)	0.000	0.027	0.010	0.009
Median Manganese (ppm)	0.000	0.367	0.010	0.056
Median Silicon (ppm)	1.346	4.228	2.794	0.742
Median Zinc (ppm)	0.000	0.152	0.008	0.025

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 11/05	% Sampling Sites 1/06 to 11/06
8.0-6.0	Unlikely to be harmful unless a high runoff of acid, Al-rich water creates a mixing zone where $Al(OH)_3$ precipitates causing acute toxicity.	38/43 = 88.4%	35/43 = 81.4%
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.	4/43= 9.3%	6/43 = 13.9%
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.	1/43 = 2.3%	2/43 = 4.7%
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.	0/43 = 0.0%	0/43 = 0.0%
4.0-3.5	This range is likely to be acutely lethal to all salmonids.	0/43 = 0.0%	0/43 = 0.0%

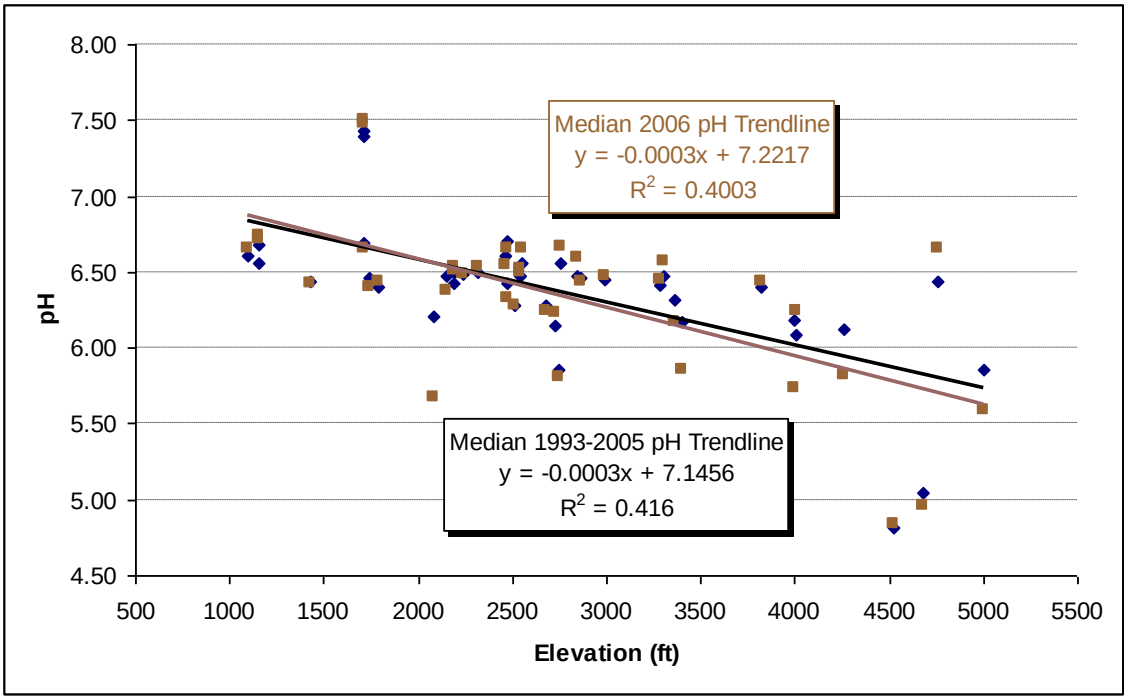


Figure 2-1. Scatter plot of median pH values versus elevation.

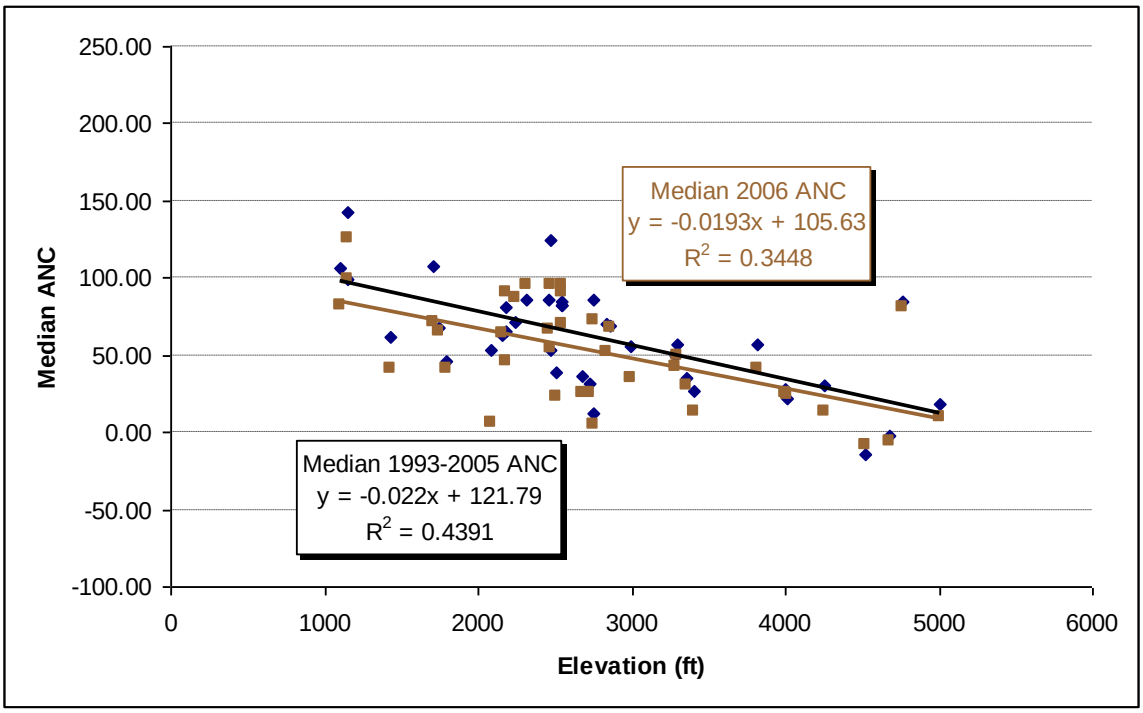


Figure 2-2. Scatter plot of median ANC values versus elevation.

Trace metals were analyzed using an ICP. Of the 230 samples analyzed, 16 had aluminum values between 100 and 200 ppb and 8 had values greater than 200 ppb. An extensive literature review points to a threshold in the 100 to 200 ppb range where the negative effects of aluminum on trout seem to 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). The EPA's 2002 National Recommended Water Quality Criteria (USEPA 2002) established criteria for the concentration of certain metals such as copper, zinc, aluminum, and iron. The freshwater criteria for aluminum are CMC (Criterion Maximum Concentration) = 750 μg/L and CCC (Criterion Continuous Concentration) = 87 μg/L. Likewise the criterion for iron is CCC = 1000 μg/L but there is no CMC criterion for iron. Unlike iron and aluminum, the CCC and CMC for metals such as zinc and copper are dependent upon water hardness. Decreasing water hardness actually increases the toxicity of these metals. The following equations were given in the 2002 Criteria in order to establish criterion concentrations.

CMC (dissolved) = exp {mA [ln (hardness)] + bA} (CF)
CCC (dissolved) = exp {mC [ln (hardness)] + bC} (CF)

Where:

mA, mC, bA, and bC = parameters found from toxicity data
hardness = water hardness in mg/L as $CaCO_3$
CF = conversion factor for converting from total recoverable metal to dissolved metal

The parameters presented in table 2-4 were established for copper and zinc for these equations.

Table 2-4. Parameters for calculating hardness dependent CMC and CCC for copper and zinc.

Paramters for Calculating Hardness-Dependent Metals Criteria					Conversion factor (CF)	
Chemical	mA	bA	mC	bC	CMC	CCC
Copper	0.9422	-1.700	0.8545	-1.702	0.960	0.960
Zinc	0.8473	0.884	0.8473	0.884	0.978	0.986

For low hardness waters like those of the Great Smoky Mountains National Park, the metal toxicity predicted by the above equations is fairly low such that there could be a significant number of exceedances. Table 2-5 displays the metals exceedances for 2003-2005 and 2006 in stream survey. It indicates that the exceedances for aluminum and ion are similar to other years. However, copper and zinc show certain reduction in exceedances.

Table 2-5 Metals exceedances for stream survey data

Trace metals	**EPA criteria (µg/L)**	**2003-2005 exceedances**	**2006 exceedances**
CMC			
Aluminum	750	2/526 = 0.4%	2/230 = 0.9%
Copper	13 (hardness =100mg/L)	410/526 = 77.9%	36/230 = 15.7%
Zinc	120 (hardness =100mg/L)	335/526 = 63.7%	53/230 = 23.0%
CCC			
Aluminum	87	117/526 = 22.2%	28/230 = 12.2%
Copper	9 (hardness = 100mg/L)	419/526 = 79.7%	37/230 = 16.1%
Fe	1000	0/526 = 0%	0/230 = 0%
Zinc	120 (hardness =100mg/L)	334/526 = 63.5%	53/230 = 23.0%

It is important to understand several aspects of the 2002 Water Quality Criteria (USEPA 1985). They are somewhat overprotective of the majority of water bodies since site specific information is very limited. The criteria also represent a threshold of unacceptable effect rather than a threshold of no adverse effect. In other words, there may indeed be some adverse

effect below the criteria. A four-day averaging period for the CCC is deemed appropriate because substantial fluctuations in concentration have more adverse effects than constant concentrations. A one-hour averaging period is appropriate for the CMC. Because of the abilities of water bodies to restore themselves, the USEPA believed an Exceedance frequency of once every three years was appropriate.

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 is performed. All accepted data are checked by laboratory QA\QC procedures.

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

Analysis	Procedure	Equipment	Method References
pH	Potentiometric	Radiometer Autotitrator	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 (NH_4^+)	Ion Chromatography	Dionex Ion Chromatograph	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-Electron Iris Intrepid II	Standard Methods 3120B EPA Method 6010B EPA Method 3005A

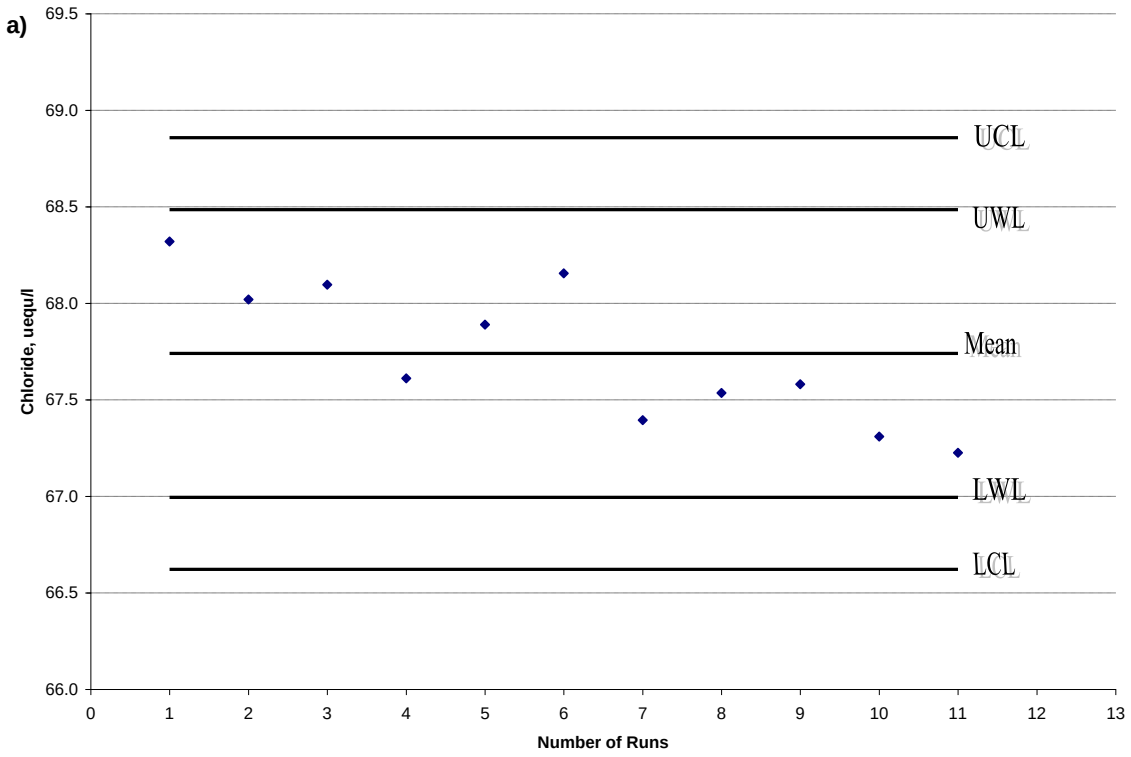
3.1 Ion Chromatography QA\QC Procedures

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 is tested for conductivity before use. The deionized water must have a conductivity of less than 1.0 μS/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 3-2 indicates very good QA\QC procedures were followed during the analyses for anions. 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). Figure 3-1 shows multiple chloride, nitrate, sulfate and ammonium measurements during several different runs. The figure shows very good precision with repeated measurements for that analyte.

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	0.999	0.999	0.999
Reagent blanks	not detected	not detected	not detected
Absolute average value in % difference in replicates	0.87% (n=4)	2.11% (n=4)	1.66% (n=4)



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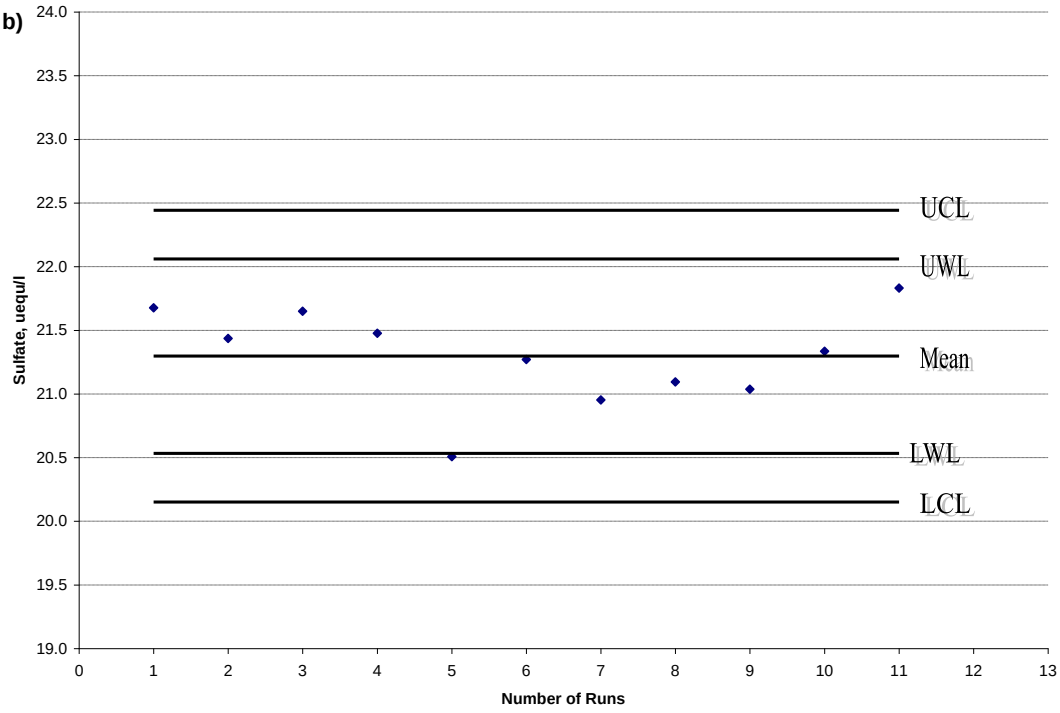
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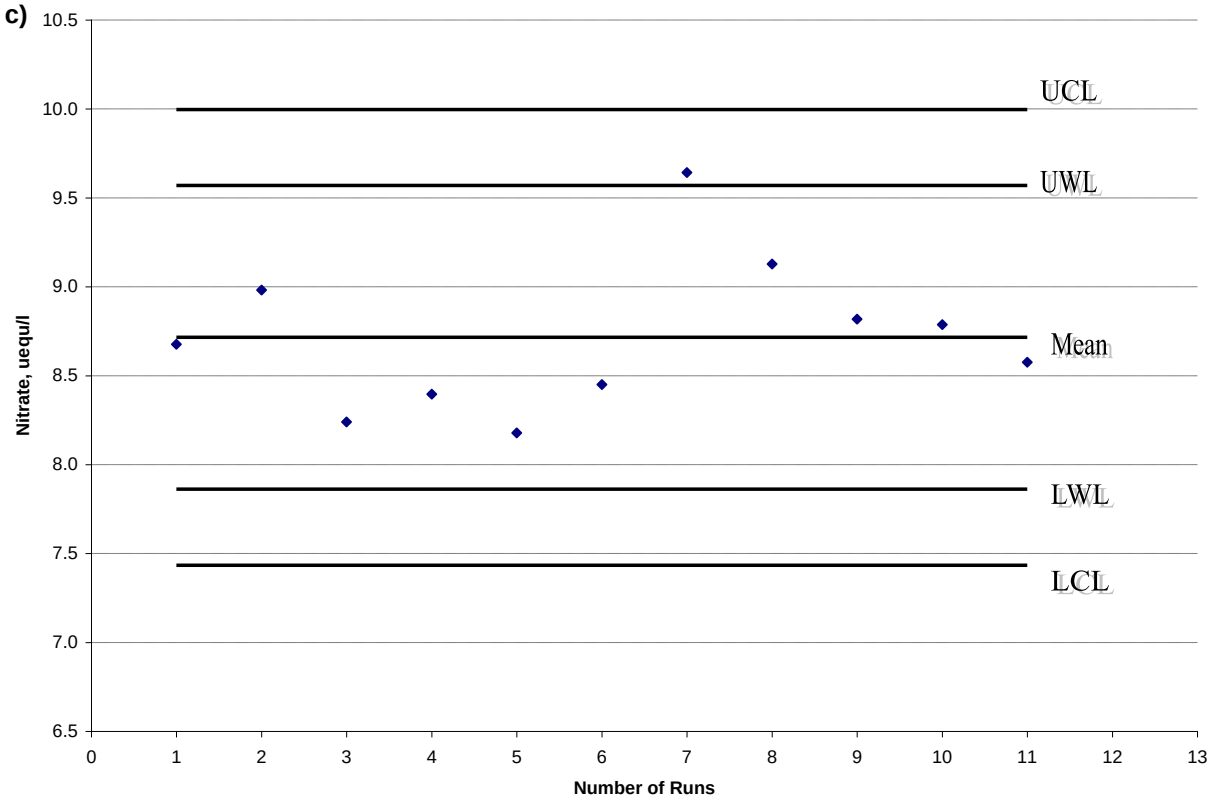
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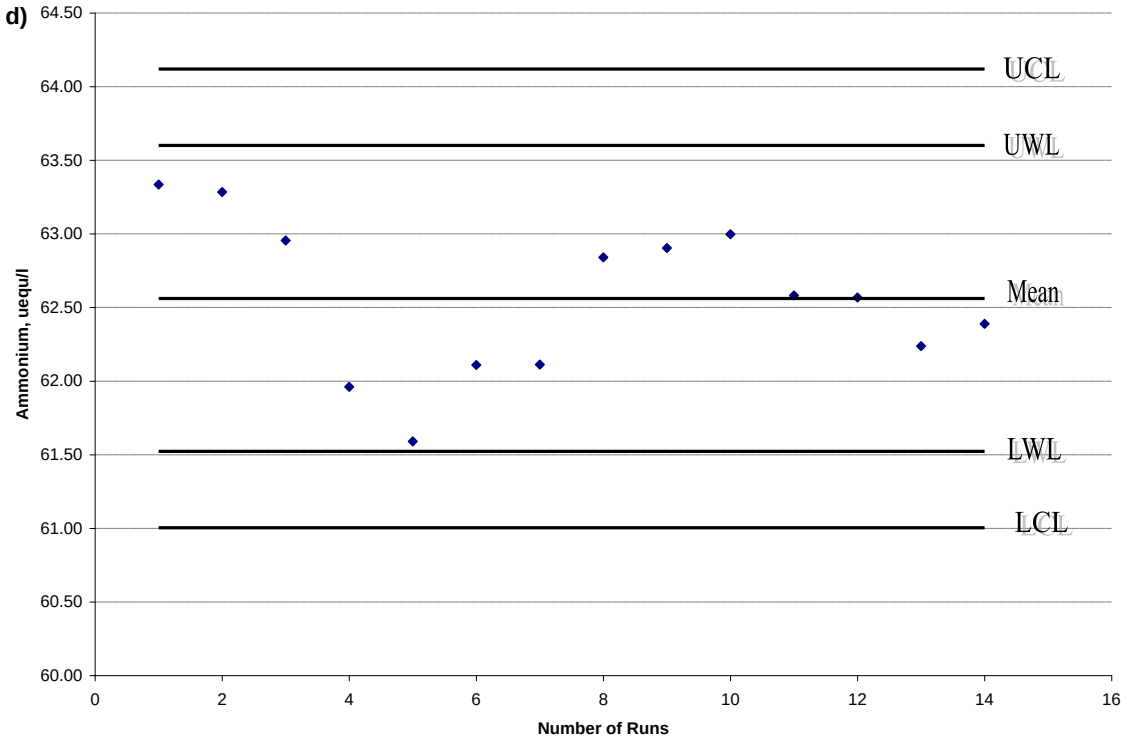

Figure 3-1. a) Chloride; (b) Sulfate; (c) Nitrate; (d) Ammonium concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (+/- 3 S.D.); UWL and LWL = upper and lower warning limits (+/- 2 S.D.).

3.2 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. There were 380 Steam Survey and Noland field samples analyzed on the ICP in 2006. An additional 215 Earmark Project field samples were analyzed concurrently with the Stream Survey and Noland samples. QA\QC procedures were performed for all 595 samples. There were 145 QA\QC samples analyzed on the ICP in 2006 (approximately 24%). Standards were prepared using certified ICP reagents and deionized (DI) water. The standard curves produced by the instrument are checked to insure linearity ($R^2 > 0.9999$) prior to sample introduction. Quality Control Check (QCC) samples were also prepared from the certified reagents and DI and run every 10 samples to ensure accuracy throughout the run. The results for the QCC samples are presented in table 3-3. Average percent errors were less than 2.5% for each element.

Table 3-3. ICP results for the prepared QCC samples.

Element	Mean Value	#	Actual Value (ppm)	% Error
Aluminum	**0.4923**	**145**	**0.5**	**1.54**
Calcium	**0.9988**	**145**	**1.0**	**0.12**
Copper	**0.4911**	**145**	**0.5**	**1.78**
Iron	**0.4965**	**145**	**0.5**	**0.69**
Potassium	**1.0043**	**145**	**1.0**	**0.43**
Magnesium	**0.9976**	**145**	**1.0**	**0.23**
Manganese	**0.4972**	**145**	**0.5**	**0.54**
Sodium	**0.4882**	**145**	**0.5**	**2.36**
Silicon	**1.0075**	**145**	**1.0**	**0.75**
Zinc	**0.4898**	**145**	**0.5**	**2.04**

A USGS trace metal sample was purchased and ran every 10 samples. The most probable values were obtained from the USGS and compared to results from the ICP. The results are presented in table 3-4. The percent errors obtained were less than 2%.

Table 3-4. ICP results for the USGS trace metal sample (T183).

Element	Mean Value	#	Actual Value (ppm)	% Error
Aluminum	**0.1291**	**70**	**0.127**	**1.66**
Calcium	**11.6407**	**70**	**11.6**	**0.35**
Copper	**0.0036***	**70**	**0.0036**	**0.94**
Iron	**0.02060**	**70**	**0.206**	**0.00**
Potassium	**2.5893**	**70**	**2.57**	**0.75**
Magnesium	**7.8648**	**70**	**7.89**	**0.32**
Manganese	**0.0485**	**70**	**0.0492**	**1.44**
Sodium	**12.8456**	**70**	**12.7**	**1.76**
Silicon	**3.8018**	**70**	**3.87**	**0.83**
Zinc	**0.0860**	**70**	**0.0864**	**0.51**

*Excludes 5 outliers with probable contamination (with outliers, mean = 0.0044, 23.2% error).

Field and reagent blanks were run. Tthe results are presented in table 3-5. Most of the values are in the very low parts per billion.

Table 3-5. ICP results for blanks.

Element	Mean Value (ppm)	#
Aluminum	**0.0041**	**82**
Calcium	**-0.0014**	**82**
Copper	**0.0041**	**82**
Iron	**0.0022**	**82**
Potassium	**0.0072**	**82**
Magnesium	**0.0000**	**82**
Manganese	**-0.0004**	**82**
Sodium	**-0.0015**	**82**
Silicon	**0.0086**	**82**
Zinc	**0.0009**	**82**

Sample replicates were prepared and run. The results are presented in table 3-6. Measured values that fell below the instrument detection limits were not included in the analysis; this accounts for the discrepancy in the number of replicate samples analyzed and reported. (Note: metals with low concentrations can cause large percent errors for small variations in

concentration).

Table 3-6. ICP results for replicates.

Element	Average Absolute Percent Difference	#
Aluminum	**9.60**	**19**
Calcium	**3.64**	**24**
Copper	**8.72**	**2**
Iron	**9.99**	**11**
Potassium	**15.58**	**23**
Magnesium	**1.42**	**24**
Manganese	**2.44**	**14**
Sodium	**2.59**	**23**
Silicon	**1.40**	**25**
Zinc	**6.27**	**11**

Sample spikes were also prepared and ran on the ICP. The average percent recoveries are presented in table 3-7. The percent recoveries of each element were all between 85% and 115% for each spike sample, which is the standard.

Table 3-7. ICP results for spikes**.**

Element	Average Percent Recovery	#
Aluminum	**98.59**	**23**
Calcium	**97.93**	**23**
Copper	**105.06**	**23**
Iron	**101.00**	**23**
Potassium	**96.47**	**23**
Magnesium	**100.04**	**23**
Manganese	**100.79**	**23**
Sodium	**97.59**	**23**
Silicon	**102.79**	**23**
Zinc	**105.75**	**23**

Minimum detection limits are determined annually. The current detection limits are shown in table 3.8.

Table 3-8. ICP Detection Limits

	2006 Detection Limits (ppm)
Aluminum	**0.021**
Calcium	**0.05**
Copper	**0.012**
Iron	**0.012**
Potassium	**0.165**
Magnesium	**0.001**
Manganese	**0.002**
Sodium	**0.041**
Silicon	**0.019**
Zinc	**0.008**

3.3 Ion Balance

Once all the analyses are performed, the results are entered into a spreadsheet and an ion balance or ion deficit for stream survey and Noland divide watershed 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 recommended guidelines. Calculation of the ion balance is embedded in the Excel spreadsheets associated with each sampling site. 5 sites over total 230 stream survey sites have ion balance above +15% or below -15%. In Noland divide watershed, the ion balance difference for lysimeter samples is normally between +20% and +30%. We consider there must exist certain anions which raised the ion difference. For other NDW samples, 5 data over total 93 samples fall out of the +\-15% range. Table 3-9 summarized the overall ion balances for streamlets, open sites and throughfall in Noland divide watershed.

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

	NE Streamlet	SW Streamlet	Open Site	Throughfall
% Ion balance	**-3.6%**	**-6.28%**	**-4.68%**	**-1.9%**
Absolute % Ion balance	**5.00%**	**7.55%**	**9.05%**	**10.53%**

3.4 USGS Round Robin Results

Once a year, the University of Tennessee Water Quality Lab participates in an 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 for the USGS Round Robin are prepared and distributed each spring and fall. The University of Tennessee Water Quality Lab generally only participates in the fall program. The Round Robin program began in 1962 from a single sample that was prepared and sent to twenty-three USGS laboratories. Currently, over two hundred USGS and non-USGS laboratories are enrolled in the USGS Round Robin.

Although 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 and storing water quality data in USGS national databases. The results from these comparisons can be used to alert participating laboratories of possible deficiencies in their analytical operations. This program provides the most probable values for the standard reference

sample. Additionally, the USGS provides Z-values and percent differences for each analyte in the reference sample.

The most probable value, UT-value, Z-value, and percent difference for each analyte are reported in Table 3-10. All University of Tennessee reported values, except copper (T-187) and potassium (P-147), had acceptable percent differences from the most probable value. The concentration of copper in the T-187 sample was below the instrument detection limit (ICP 2006); the concentration of potassium in the P-47 sample was just above the instrument detection limit (ICP 2006).

Table 3-10. Round Robin Results. (All concentration data are given in ppm, and conductivity is given in μS/cm).

Sample	Analyte	MPV*[1]	UT-results	Z-value	% difference
T-187	Al	0.0629	0.0651	0.56	3.58
	Ca	3.90	3.94	0.28	0.92
	Cu	0.0020	0.0032	8.9	58.04
	Fe	0.0515	0.0578	1.02	12.31
	Mg	12.8	13.1	0.67	2.02
	Mn	0.0060	0.0070	3.72	17.08
	K	8.70	8.80	0.35	1.15
	SiO_2	6.38	6.47	0.26	1.46
	Na*[2]	18.0	18.15	-	0.87
	Zn	0.0122	0.0127	0.64	4.25
P-47	Conductivity	20.0	18.6	-01.36	-6.95
	pH	6.65	6.3	-1.15	-5.26
	Cl	0.280	.255	-0.34	-13.78
	SO_4	0.190	0.168	-0.52	-11.58
	Ca	1.45	1.38	-1.47	-4.97
	Mg	0.123	0.123	0.00	0.00
	K	0.190	0.293	5.72	54.21

	Na*[3]	**1.76**	**1.56**	**-**	**11.36**
N-92	**NO_3- + NO_2 as N*[3]**	**1.41**	**1.40**	**-**	**0.71**

1. Most probable values in the overall results.
2. Not reported to USGS.
3. Misreported to USGS (Na: decimal error, NO_3: conversion error).

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.

In last year, we did not lose any chemistry sample for stream survey. However, four NDW grab samples lost from laboratory, and one sample is not sufficient for all chemistry analysis. 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 2006, we lost two records for water weight from open site and througfall.

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, destroy by birds and bears, and malfunctioning units. We estimate that 75% of the conductivity, temperature and pH was captured due to instrumental problems in 2006. Stream flow measurements are interrupted on occasion due to freezing of the flumes' stilling wells. We estimate that better than 85% 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.

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

Stephan, C.E., Mount, D.I., Hansen, D.J., Gentile, J.H., Chapman, G.A., and Brungs, W. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses*. USEPA Office of Research and Development, Environmental Research Laboratories, Duluth, MN, Narragansett, RI, Corvallis, OR, 1985.

USEPA . *National Recommended Water Quality Criteria: 2002*. Office of Water; 2002. EPA-822-R-02-047. <http://www.epa.gov/waterscience/pc/revcom.pdf> (Aug. 2004).

USEPA . *2003 Draft Update of Ambient Water Quality Criteria for Copper*. Office of Water, 2003. EPA-822-R-03-026. < http://www.epa.gov/waterscience/criteria/copper/pdf/master.pdf > (Sept. 2004).

NOAA, 2006 *Local Climatological Data Annual Summary with Comparative Data* http://www1.ncdc.noaa.gov/pub/orders/286EEBB7-C367-DD74-BDEB-C1A90260E243.PDF (April, 2007)