

Smoky Mountains Water Quality Annual Report for 2005

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This report describes for water quality monitoring in the Great Smoky Mountains National Park for calender year (CY) 2005 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 2005, the estimated amount of total inorganic nitrogen entering the Noland Divide Watershed (NDW) as throughfall was 1191 equivalents of nitrogen per hectare per year (eq/ha/yr), and 423 (eq/ha/yr) was collected as wet-only precipitation (see Figure 1-1). These deposition rates were slightly lower than last year's totals but very close to the 12 year average deposition rates recorded since the project began in 1991.

The estimated amount of sulfate entering the NDW as throughfall was 2029 (eq/ha/yr), and 489 (eq/ha/yr) as wet-only precipitation (Figure 1-2). These deposition rates were above the 12 year average deposition rates for sulfate as throughfall, but lower than average sulfate deposition measured as wet-only precipitation. 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 throughfall collection methods were changed on 6/9/05 and followed a combination of European standards (Appendix 1). However, the total values are based on the original methods.

The annual rainfall amount collected during 2004 was 200 cm, while surrounding lowland areas such as Knoxville, TN generally average around 98 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).

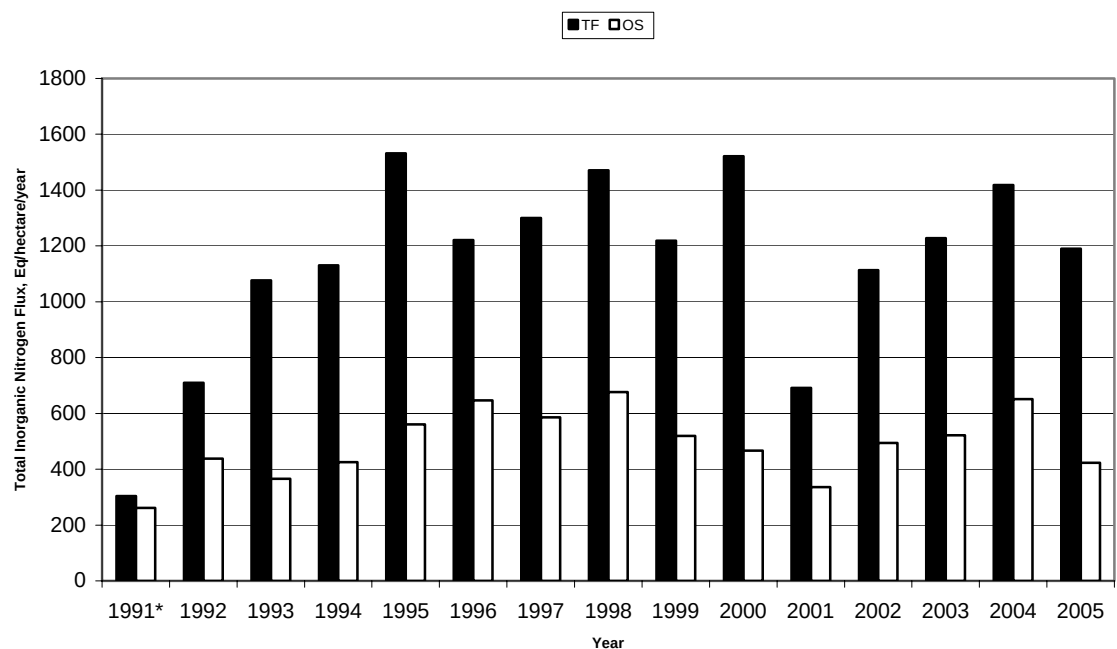


Figure 1-1. Total inorganic nitrogen deposition entering the NDW as throughfall and wet-only precipitation.

*The collections in 1991 started in June, and represent only half of the years total deposition rates.

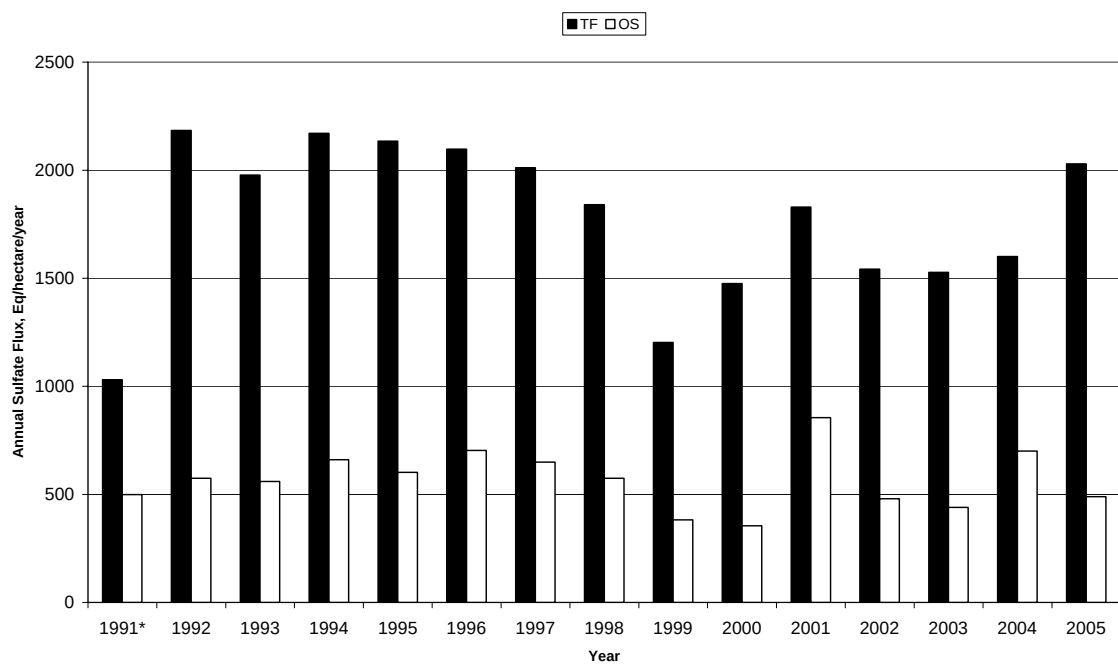


Figure 1-2. Total sulfate entering the NDW as throughfall and wet-only precipitation.
 *The collections in 1991 started in June, and represent only half of the years total deposition rates.

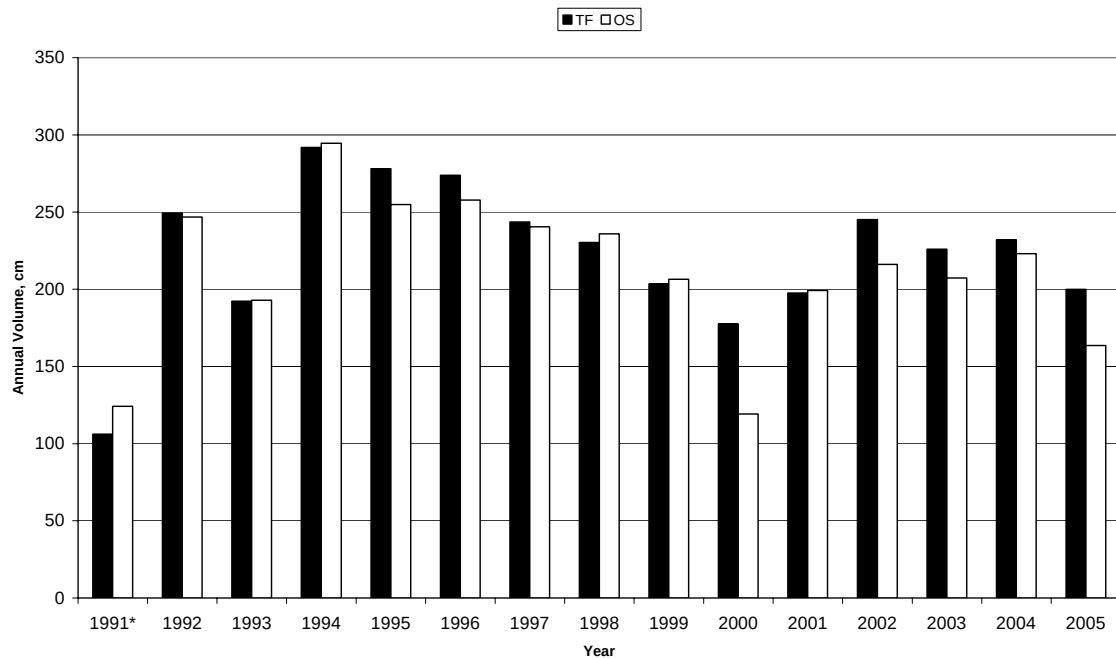


Figure 1-3. Total annual throughfall and wet-only precipitation volumes entering the NDW.
 *The collections in 1991 started in June, and represent only half of the total deposition rates.

1.2 Soil Lysimeter Chemistry

Soil water chemistry is collected monthly from 12 lysimeters located at 3 different depths within the NDW. The annual volumes for the upper, middle, and lower lysimeters were 975, 5342, and 7090 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	3.43	45.40
	Average	4.05	71.53
	Maximum	4.53	106.90
Middle Lysimeter	Minimum	4.01	27.10
	Average	4.36	47.36
	Maximum	4.66	62.30
Lower Lysimeter	Minimum	4.46	34.50
	Average	4.51	43.43
	Maximum	4.62	57.50

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

		Cl^-	NO_3^-	SO_4^{2-}
Upper Lysimeter	Minimum	17.93	66.08	57.00
	Average	33.34	157.89	106.33
	Maximum	59.68	247.40	171.22
Middle Lysimeter	Minimum	5.04	73.54	46.25
	Average	20.80	147.93	83.96
	Maximum	41.05	279.66	179.53
Lower Lysimeter	Minimum	3.30	112.27	70.69
	Average	16.07	167.47	75.23
	Maximum	42.21	265.85	80.85

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

		Na^+	K^+	Mg^{2+}	Ca^{2+}
Upper Lysimeter	Minimum	16.60	3.60	23.21	26.09
	Average	33.28	41.08	37.51	62.11
	Maximum	63.52	73.01	54.95	85.94
Middle Lysimeter	Minimum	10.92	4.46	18.74	19.31
	Average	21.65	6.50	28.24	28.50
	Maximum	37.42	8.43	37.33	47.54
Lower Lysimeter	Minimum	13.07	5.34	24.17	27.74
	Average	18.96	8.43	31.24	40.84
	Maximum	23.57	9.85	43.76	51.28

2.0 Stream Survey Results

The following analyses utilize the chemistry data of collected samples from forty-five sites within the GRSM. The data set includes samples collected from thirty-two sites during six stream surveys in January, March, May, July, September and November 2005 and eleven samples collected from the Hazel Creek watershed in March and September of 2005. Throughout the following text, comparisons will be made between the data collected in 2005 and previous data collected from October 1993 to November 2004. In 2004, the number of stream survey sites was decreased from 90 to 43. The comparisons below include data from only the 43 remaining sites.

Table 2-1 shows descriptive statistics of the water quality constituents for the 1993 to 2003 data set for the previous 90 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 2005 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 2005 and 1993-2004 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 2005 data changes slightly from the 1993-2004 data set. The 2004 and 2005 data has about nine percent fewer 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 2005 and 1993-2004 data plotted by

elevation.

Figure 2-2 is a scatter plot of median ANC values (excluding Cades Cove sites) for the 2005 and 1993-2004 data plotted by elevation.

The plots show that overall median pH and ANC values decrease with increasing elevation.

Table 2-1. Descriptive statistics of 1993-2003 median water quality values for all sites.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation
Median pH	4.820	7.472	6.395	0.412
Median ANC (µeq/L)	-14.831	976.840	100.317	192.233
Median Conductivity (µS/cm)	10.415	96.300	19.883	17.588
Median Chloride (µeq/L)	12.282	22.756	15.622	2.053
Median Nitrate (µeq/L)	0.000	56.674	17.887	16.571
Median Sulfate (µeq/L)	14.414	246.963	43.476	43.455
Median Sodium (µeq/L)	17.904	69.577	40.833	10.160
Median Ammonium µ (eq/L)	0.000	0.000	0.000	0.000
Median Potassium (µeq/L)	3.341	16.076	10.483	2.894
Median Magnesium (µeq/L)	15.967	174.691	39.146	33.105
Median Calcium (µeq/L)	29.225	761.000	92.282	150.518
Median Aluminum (ppm)	0.022	0.227	0.082	0.044
Median Copper (ppm)	0.000	0.020	0.007	0.005
Median Iron (ppm)	0.005	0.060	0.029	0.017
Median Manganese (ppm)	0.000	0.181	0.009	0.032
Median Silicon (ppm)	0.962	4.958	2.385	0.843
Median Zinc (ppm)	0.013	0.084	0.031	0.017

Table 2-2. Descriptive statistics of 2005 median water quality values for all sites.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation
Median pH	4.739	7.654	6.384	0.607
Median ANC (µeq/L)	-6.190	700.991	72.275	101.738
Median Conductivity (µS/cm)	7.992	125.3000	21.4654	13.0583
Median Chloride (µeq/L)	7.951	17.340	12.251	2.238
Median Nitrate (µeq/L)	7.805	59.067	23.121	13.862
Median Sulfate (µeq/L)	16.499	387.181	54.037	57.734
Median Sodium (µeq/L)	17.106	66.632	36.635	10.295
Median Ammonium (µeq/L)	0.000	0.000	0.000	0.000
Median Potassium (µeq/L)	5.274	18.019	11.680	3.285
Median Magnesium (µeq/L)	16.244	186.307	43.106	36.925
Median Calcium (µeq/L)	33.635	806.799	99.186	147.607
Median Aluminum (ppm)	0.005	0.575	0.057	0.085
Median Copper (ppm)	0.001	0.029	0.004	0.006
Median Iron (ppm)	0.009	0.036	0.023	0.006
Median Manganese (ppm)	0.001	0.340	0.013	0.050
Median Silicon (ppm)	1.339	4.528	2.592	0.709
Median Zinc (ppm)	0.000	0.049	0.009	0.007

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 11/04	% Sampling Sites 1/05 to 12/05
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.	35/42 = 83.3%	36/42 = 85.7%
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.	3/42 = 7.1%	4/42 = 9.5%
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.	1/42 = 2.3%	2/42 = 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.	0/42 = 0.0%	0/42 = 0.0%
4.0-3.5	This range is likely to be acutely lethal to all salmonids.	0/42 = 0.0%	0/42 = 0.0%

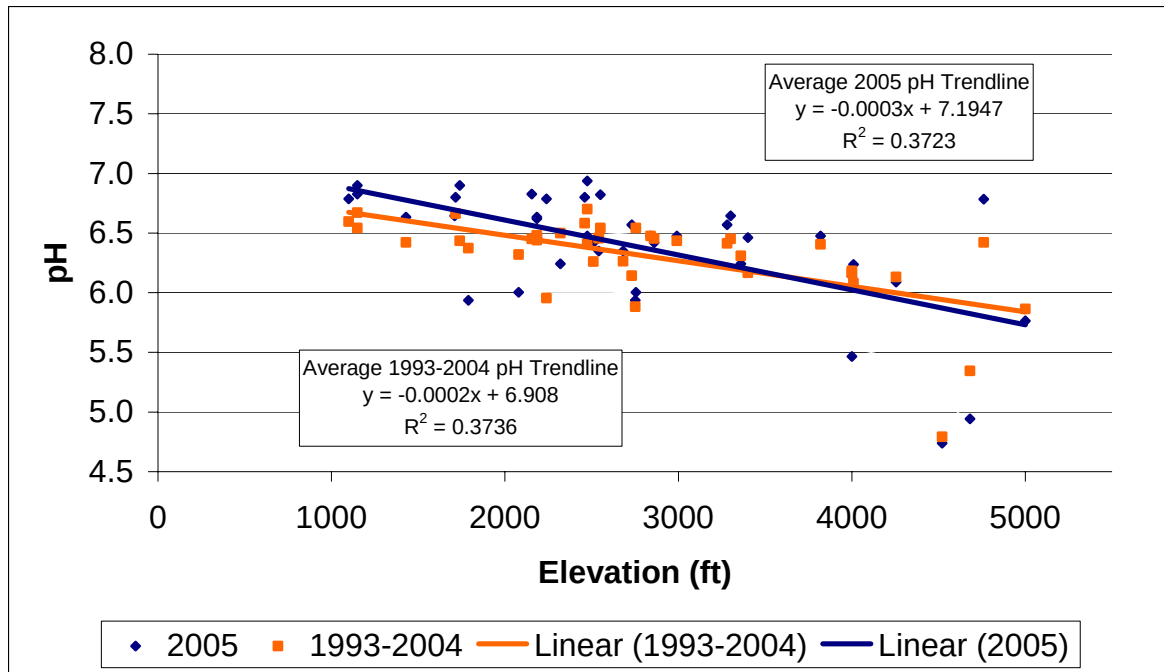


Figure 2-1. Scatter plot of median pH values versus elevation.

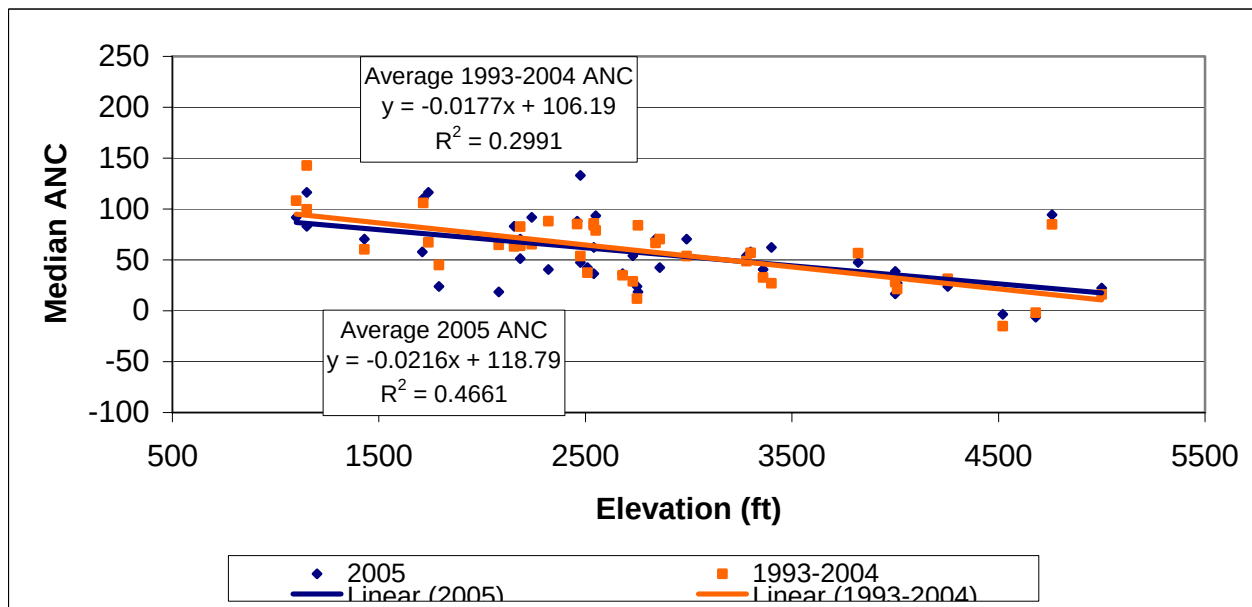


Figure 2-2. Scatter plot of median ANC values versus elevation.

Trace metals were analyzed using an ICP. Of the 211 samples analyzed, 17 had aluminum values between 100 and 200 ppb and 11 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.

$$\text{CMC (dissolved)} = \exp \{m_A [\ln (\text{hardness}) + b_A] \} (\text{CF})$$

$$\text{CCC (dissolved)} = \exp \{m_C [\ln (\text{hardness}) + b_C] \} (\text{CF})$$

Where:

m_A , m_C , b_A , and b_C = parameters found from toxicity data

hardness = water hardness in mg/L as CaCO₃

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.

Parameters 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. The following table displays the metals exceedances for data from the 2005 Stream Survey.

Table 2-5. Metals exceedances for 2005 stream survey data.

	Copper		Zinc		Aluminum		Iron
	CMC	CCC	CMC	CCC	CMC	CCC	CCC
# exceedances	114	120	22	22	2	41	0
# events	210	210	210	210	210	210	210
% exceedance	54.3	57.1	10.5	10.5	0.9	19.5	0

The data used by the EPA to form the hardness-dependent equations were in the 20- 400 mg/l hardness range. In the past, EPA has allowed the criterion concentrations to be calculated as if the hardness was 25 mg/l for waters with hardness less than 25 mg/l as CaCO₃. Recently EPA has decided that capping hardness at this lower end should not be allowed because it might result in criteria that provide less protection than intended (USEPA 2002).

In the hardness-dependent equations, hardness is used as a surrogate parameter for the influence of factors such as calcium, magnesium, carbonate, and pH (Charles Delos, USEPA, personal communication, Sept. 3, 2004). However, the ability to extrapolate criterion

concentration values for such low values of hardness still remains questionable. Therefore, metals concentrations will be compared in this report to the results of the hardness-dependent equations for both the measured hardness level and 20 mg/l as CaCO₃. The table below shows metals exceedances for the 2005 Stream Survey data when a hardness of 20 mg/l as CaCO₃ is used.

Table 2-6. Metals exceedances for 2005 stream survey data using hardness = 20 mg/l as CaCO₃.

	Copper		Zinc		Aluminum		Iron
	CMC	CCC	CMC	CCC	CMC	CCC	CCC
# exceedances	96	112	11	11	2	41	0
# events	210	210	210	210	210	210	210
% exceedance	45.7	53.3	5.2	5.2	0.9	19.5	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 are performed.

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 $\mu\text{S}/\text{cm}$.

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 3-2 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 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⁻	NO₃⁻	SO₄²⁻
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	1.69% (n=4)	1.62% (n=4)	4.10% (n=4)

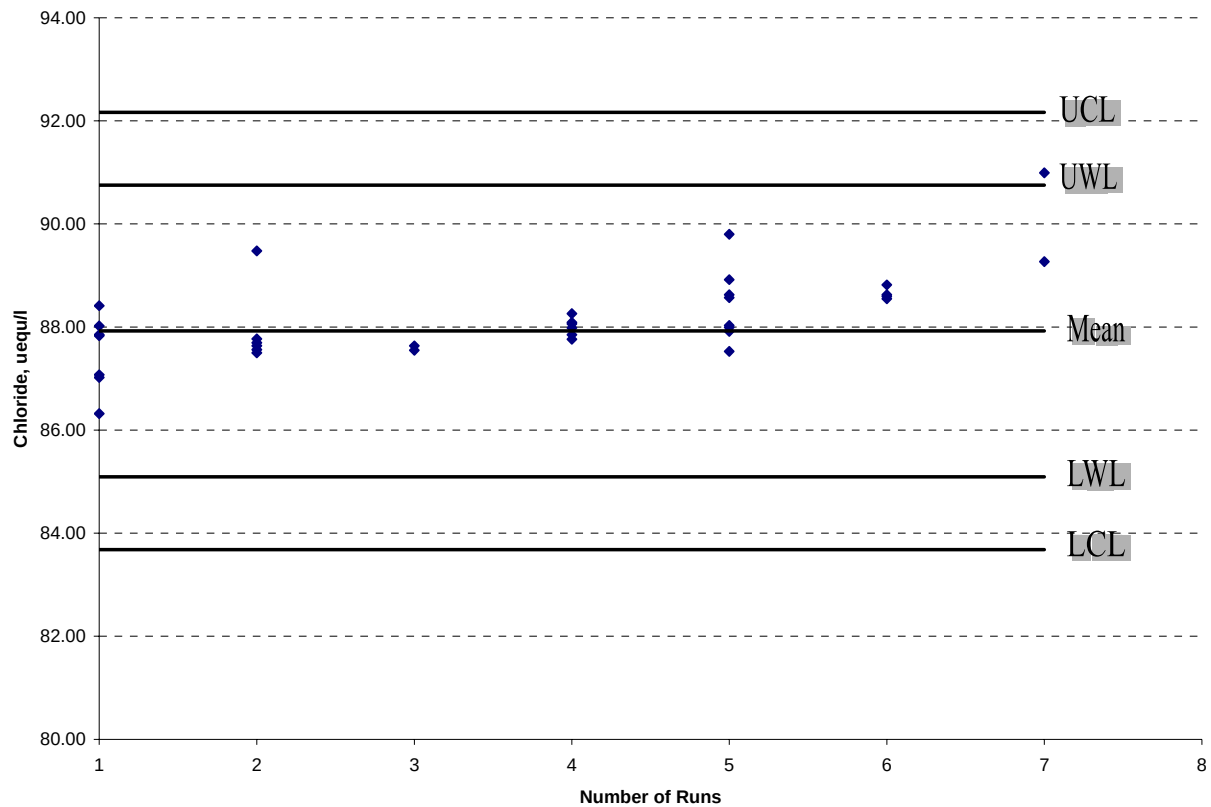


Figure 3-1. Chloride concentrations made on laboratory check sample over multiple runs. UCL and LCL = upper and lower control limits (± 3 S.D.); UWL and LWL = upper and lower warning limits (± 2 S.D.).

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 443 field samples and 169 QA/QC samples (about 35%) analyzed on the ICP in 2004. 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 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 4% for each element.

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

Element	Mean Value (ppm)	#	Actual Value (ppm)	% Error
Aluminum	0.487	74	0.5	2.55
Calcium	1.993	74	2.0	0.37
Copper	0.489	74	0.5	2.15
Iron	0.987	74	1.0	1.31
Potassium	0.994	74	1.0	0.60
Magnesium	1.999	74	2.0	0.03
Manganese	0.489	74	0.5	2.20
Sodium	0.999	74	1.0	0.13
Silicon	0.995	74	1.0	0.51
Zinc	0.481	74	0.5	3.81

A USGS trace metal sample was purchased and ran every 25 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 all values being less than four percent.

Table 3-6. ICP results for the USGS trace metal sample (T179).

Element	Mean Value (ppm)	#	Actual Value (ppm)	% Error
Aluminum	0.058	40	0.052	11.48
Calcium	18.862	40	18.900	0.20
Copper	0.004	40	0.004	7.30
Iron	0.127	40	0.125	1.91
Potassium	1.464	40	1.400	4.60
Magnesium	4.579	40	4.590	0.23
Manganese	0.045	40	0.044	2.63
Sodium	27.398	40	26.200	4.57
Silicon	6.902	40	6.960	0.83
Zinc	0.009	40	0.009	10.49

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	0.021	30
Calcium	0.023	30
Copper	0.009	30
Iron	0.010	30
Potassium	0.035	30
Magnesium	0.000	30
Manganese	0.002	30
Sodium	-0.034	30
Silicon	0.030	30
Zinc	0.003	30

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 iron which had very low concentrations, which can cause large percent errors for small variations in concentration.

Table 3-8. ICP results for replicates.

Element	Average Absolute Percent Difference	#
Aluminum	10.32	6
Calcium	4.88	6
Copper	21.87	6
Iron	27.68	6
Potassium	12.13	6
Magnesium	2.74	6
Manganese	2.25	6
Sodium	2.39	6
Silicon	1.20	6
Zinc	4.34	6

Sample spikes were also prepared and ran on the ICP. The average percent recoveries are presented in table 3-9. The percent recoveries of each element were all between 85% and 115% for each spike sample, which is the standard.

Table 3-9. ICP results for spikes.

Element	Average Percent Recovery	#
Aluminum	92.21	19
Calcium	97.76	19
Copper	95.89	19
Iron	97.13	19
Potassium	93.45	19
Magnesium	99.44	19
Manganese	95.86	19
Sodium	100.84	19
Silicon	96.76	19
Zinc	95.68	19

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 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 recommended 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 3-10. Average ion balances for both streamlets, precipitation and throughfall.

	NE Streamlet	SW Streamlet	Open Site	Throughfall
% Ion balance	1.71%	3.06%	6.28%	-0.85%
Absolute % Ion balance	4.76%	6.11%	11.57%	11.83%

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 3-11. All University of Tennessee reported values, except Aluminum, Silicon and Copper, had an acceptable percent difference from the most probable value. The value submitted to the USGS for Silicon was not converted into Silicon dioxide as specified by USGS. Once converted into Silicon dioxide, the percent difference is -2.5%. The sample introduction of the ICP was responsible for the large percent difference in Aluminum and Copper. After receiving the results from the Round Robin survey, the nebulizer and sample introduction intake tubing were inspected under a microscope. Impacted dust was found in the intake tubing. The dust contributed to Copper contamination, and drifting values for all metals analyzed by the ICP. This problem was resolved by replacing the intake tubing. The ICP QA/QC for T-183 samples (after replacement of intake tubing) has produced percent differences less than 5% for all metals.

Table 3-11. Round Robin Results. All concentration data are given in ppm, and conductivity is given in $\mu\text{S}/\text{cm}$.

Sample	Analyte	MPV ¹	UT-results	Z-value	% difference
T-183	Al	0.127	0.2181	10.24	71.79
	Ca	11.6	11.5	-0.2	-0.73
	Cu	0.00306	0.042	**	**
	Fe	0.206	0.1961	-0.64	-4.79
	Mg	7.89	7.36	-1.55	-6.69
	Mn	0.0492	0.05297	2.42	7.66
	K	2.57	2.54	-0.34	-1.26
	SiO ₂	8.27	3.7725	-10.04	-54.38
	Na	12.7	13.09	0.74	3.08
	Zn	0.086	0.083	-0.66	-3.98
P-43	Conductivity	4.79	4.13	-0.62	-8.93
	pH	6.15	5.94	-0.5	-3.41
	Cl	0.28	0.255	-0.34	-13.78
	SO ₄₂₋	0.25	0.224	-0.5	-10.4
	Ca	0.134	0.1415	0.22	5.6
	Mg	0.17	0.1672	-0.18	-1.65
	K	0.164	0.1175	-2.33	-28.35
	Na	0.115	0.0904	-1.12	-21.39
N-84	NO ₃ - + NO ₂ as N	1.17	1.167	-0.07	-0.26
	NH ₃ as N	1.17	1.329	2.15	13.59

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 2005, we did not lose any collectors for throughfall due to bear damage.

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 80% of the conductivity and temperature was captured due to instrumental problems in 2005. Also, the pH electrodes do appear to sometimes have a drift in the readings. It's difficult to determine exactly how much data may be invalid due to drift but we estimate no more than about 25%. Stream flow measurements are interrupted on occasion due to freezing of the flumes' stilling wells. We estimate that better than 90% 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 samples are collected except in the rare occasion when the sites are inaccessible or the streams are dry. Usually over 99% of all samples are obtained. However, some samples were lost, damaged, or unattainable this year. 98% of the stream survey samples were collected in 2005.

4.0 References

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5.0 Appendix

Preliminary Survey of Soil Lysimeter Data at Noland Divide

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The National Park Service (NPS) has been collecting soil lysimeter data at Noland Divide from 1992 through the present. Soil water samples are collected at 3 layers within the soil horizon. The soil water samples are collected in approximately one month increments and transported to the University of Tennessee for laboratory analysis. The water samples are analyzed for pH, conductivity, and various cations, anions, and trace metals.

Johnson and Lindberg characterized the soil at the Noland Divide site as consisting of a 4 cm thick Oi + Oe horizon of needles and leaves, a 4 cm thick Oa horizon of mucky humus, an 8 cm thick A horizon of dark, reddish-brown, mucky loam, a 27 cm thick Bw horizon of dark brown, sandy loam, a 35 cm thick Cb horizon of dark, yellowish-brown loam, a 20+ cm thick C horizon of olive-brown, loamy sand, and underlying sandstone bedrock. The shallowest lysimeter (ID # 4135) is placed in the A horizon, the intermediate lysimeter (ID # 4145) is placed in the Bw horizon, and the deepest lysimeter (ID # 4155) is placed in the Cb horizon.

The purpose of this report is to explore the soil lysimeter data. This is the first step in assessing the value of the lysimeter and how the collected data can be used. If the data are indeed significant, we must determine how they may be applied. The lysimeter assessment may indicate other tests **that** might be more useful.

The lysimeter data trends were explored statistically and graphically. A linear regression

was performed on the parameters to determine the significance of the trends throughout the soil profile. Trends were considered to be significant with respect to time if they had a P-value of less than or equal to 0.05. Time trends for each parameter are included at the end of the report. Data plots were used to evaluate depth trends. An Analysis of Variance (ANOVA) was performed on aluminum and sulfate data to determine if the concentrations were significantly different for the three soil layers. The layers are essentially of the same population, meaning there is statistically no significant difference between layers, if the P-value is greater than or equal to 0.05.

RESULTS

The first parameter examined was pH. pH has shown a decreasing trend in each strata with a range of 0.1-0.25 pH units decrease over the thirteen year period. These trends are statistically significant for the lower 2 layers, but not the top layer. pH increases with depth, presumably due to the buffering capacity of the soil. The decrease in soil pH at lower depths is in contrast to the approximate 0.1 pH unit increase ($p = 0.086$) in wet only precipitation at Noland Divide. The reason for the slow soil pH decline is unknown. Table 1 compares soil water and atmospheric deposition pH and shows that the pH of the shallowest soil depth is about 0.6 units lower and has 38.2 $\mu\text{eq/L}$ more H^+ than the throughfall pH. If this pH drop were due to oxidation of the ammonia, than 31.6 $\mu\text{eq/L}$ of this H^+ increase could be accounted for.

The decrease in pH also means that the hydrogen ion concentration has increased within each layer. The trend is considered statistically significant throughout the profile. Hydrogen ion concentration decreases with depth, which is consistent with pH depth trends.

Conductivity has shown differing trends over the soil depth. Conductivity has decreased in the top strata, but has increased slightly in the lower two layers. Conductivity decreases with depth. The trends are not statistically significant in any of the three layers.

Calcium is an important cation for vegetation. Calcium has shown a decreased concentration in all three layers of the soil, although the period of record is only since November 1998. Calcium concentrations are highest in the shallowest layer. One anomaly is that the middle layer has a lower concentration than the lower layer. However, none of the trends are statistically significant over the time interval.

The two primary anions of interest are nitrate and sulfate. Nitrate concentration is slightly increasing with time, although the time trends are not statistically significant. Nitrate concentration is highest in the top layer and lowest in the middle layer, which may be consistent with plant uptake.

Sulfate concentration is decreasing over time almost identically within each layer of the soil. The sulfate concentration trends are consistent with the decrease in atmospheric deposition. The ANOVA test yielded a P-value of 0.44, implying there is no significant difference between layer concentrations and each layer is statistically of the same population. Of the major ions, the sulfate throughfall concentration most closely matches the soil water, which could be expected given that the sulfate should not be biologically active.

Trends for aluminum, copper, and zinc concentrations are not significant and experience some extreme outliers. Trace metal concentrations have only been collected since 2003 and do not represent the same period of study as the other parameters. An ANOVA test on aluminum gave a P-value of 0.72, implying there is no significant difference between layer concentrations and each layer was statistically from the same population.

Table 1 summarizes the mean species concentrations at the three lysimeter depths, as well as in the wet only and throughfall deposition at Noland Divide. The lysimeter concentrations match throughfall concentrations more closely than wet only precipitation, which is expected because the lysimeter is under the tree canopy.

CONCLUSIONS

The lysimeter soil water chemistry data do show interesting time and depth trends. Except for possibly the declining soil water pH, the observed trends do not seem surprising. The significance of the soil water chemistry data on vegetation and nutrient cycles must be determined by others. The significance on water quality, or soil adsorptive capacity, is not immediately clear and will require further literature review.

Table 1. Mean Concentration (Standard Deviation)

Sample	pH (pH units)	H ⁺ (µeq/L)	Conductivity (uS/cm ²)	Ca ²⁺ (µeq/L)	NO ₃ ⁻ (µeq/L)	SO ₄ ²⁻ (µeq/L)	Al ³⁺ (ppm)	Cu ²⁺ (ppm)	Zn ²⁺ (ppm)
4135	4.02	114.32	66.88	59.28	135.46	97.11	1.05	8.76E-03	0.19
	0.27	70.56	33.37	79.58	130.80	52.74	0.47	9.07E-03	0.14
4145	4.39	46.86	37.10	31.71	72.18	99.40	0.98	5.73E-03	0.13
	0.27	26.11	15.04	19.02	55.12	36.31	0.26	7.08E-03	0.13
4155	4.46	36.50	33.67	40.18	79.85	92.81	1.00	9.68E-03	0.11
	0.17	12.74	8.65	26.10	36.82	22.21	0.16	1.12E-02	0.06
Wet only ¹	4.71	25.96	12.99	8.67	11.80 ²	27.28	0.081	0.011	0.064
Throughfall ¹	4.62	76.11	43.18	41.58	42.55 ²	85.79	0.076	0.010	0.120

¹ Weighted average

² Weighted average ammonium is 14.19 and 15.79 µeq/L in wet only and throughfall respectively given, total nitrogen of 25.99 and 58.34 µeq/L nitrogen as nitrate.

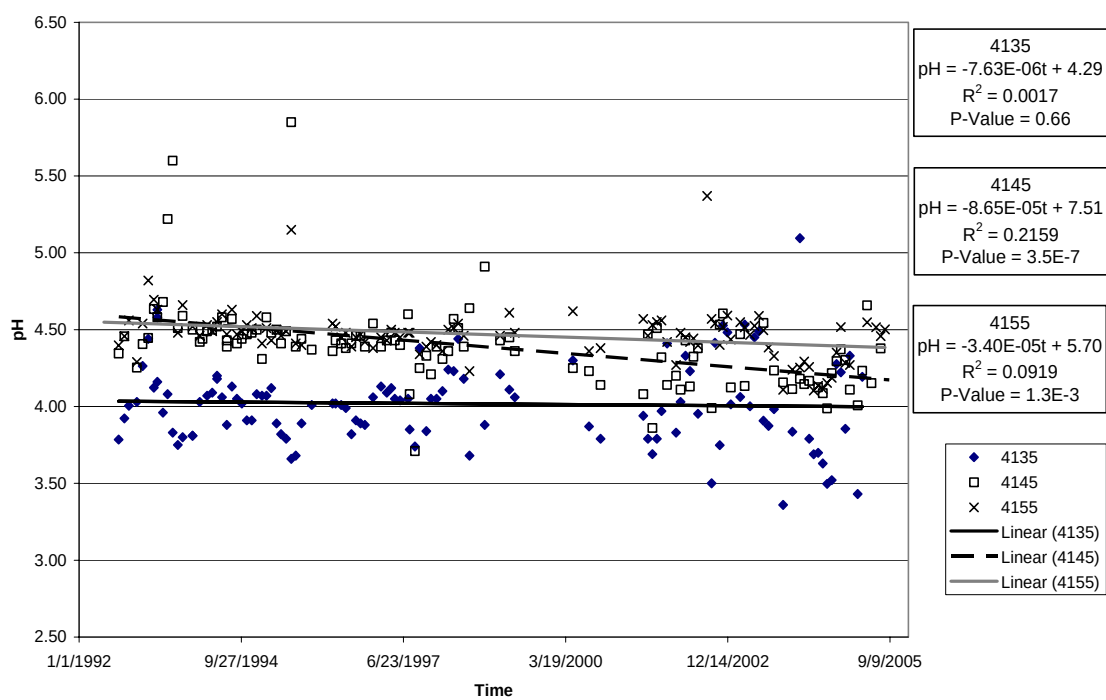


Figure 1. pH vs. Time for Noland Divide lysimeter data

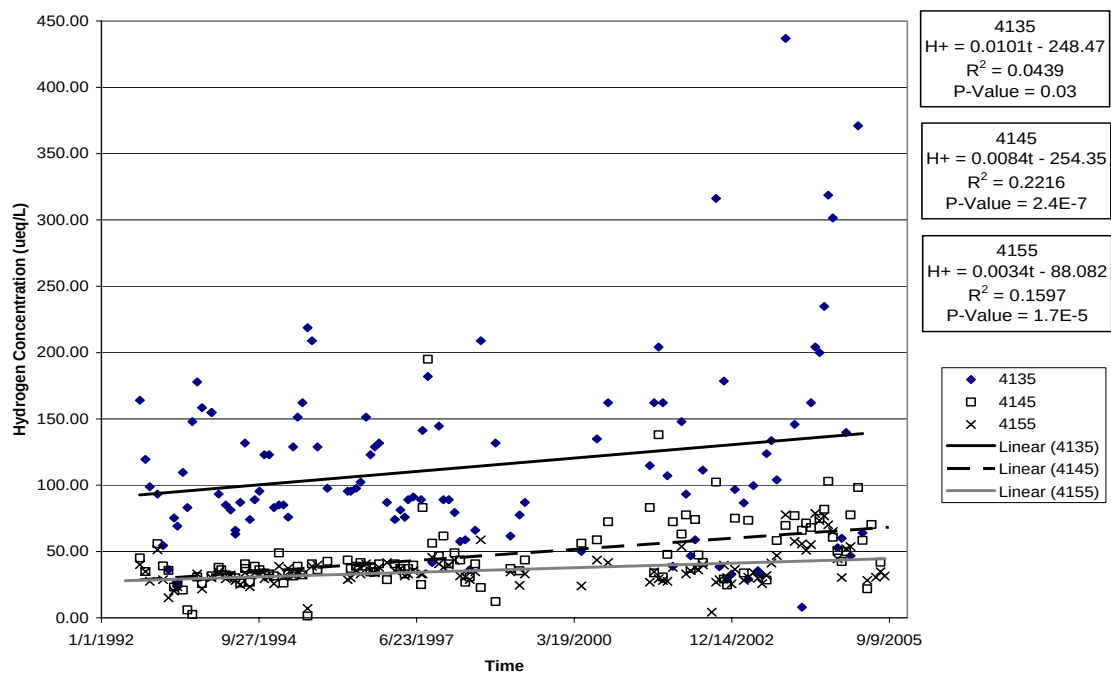


Figure 2. Hydrogen Ion Concentration vs. Time for Noland Divide lysimeter data

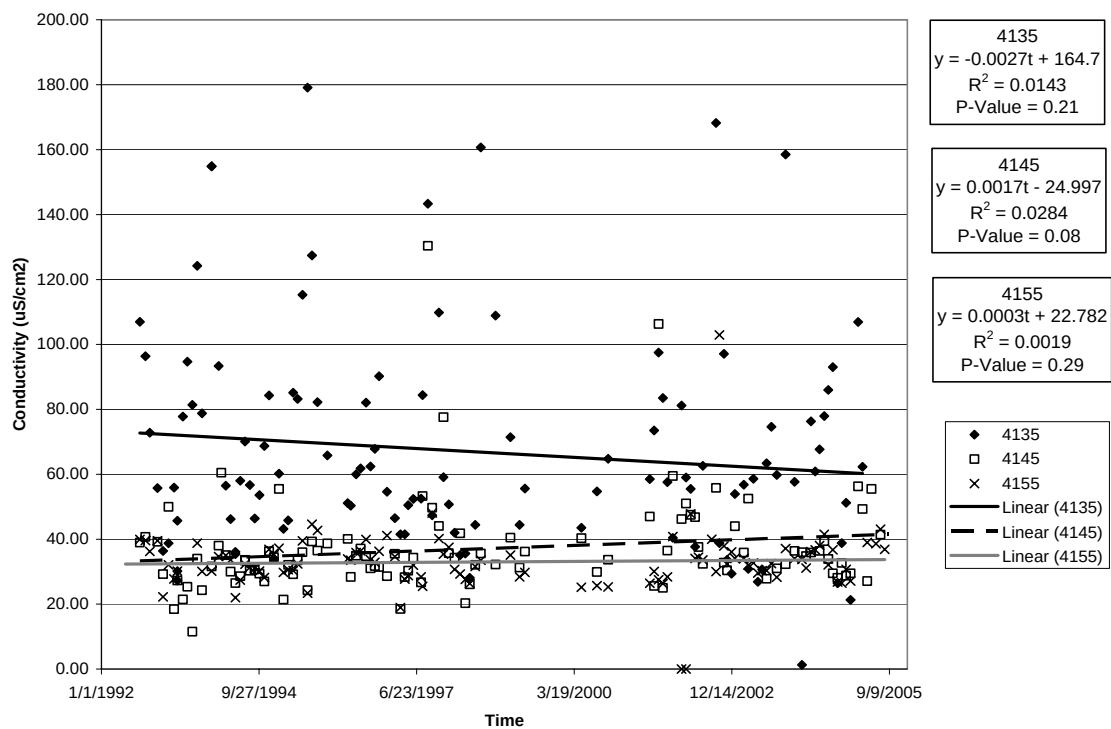


Figure 3. Conductivity vs. Time for Noland Divide lysimeter data

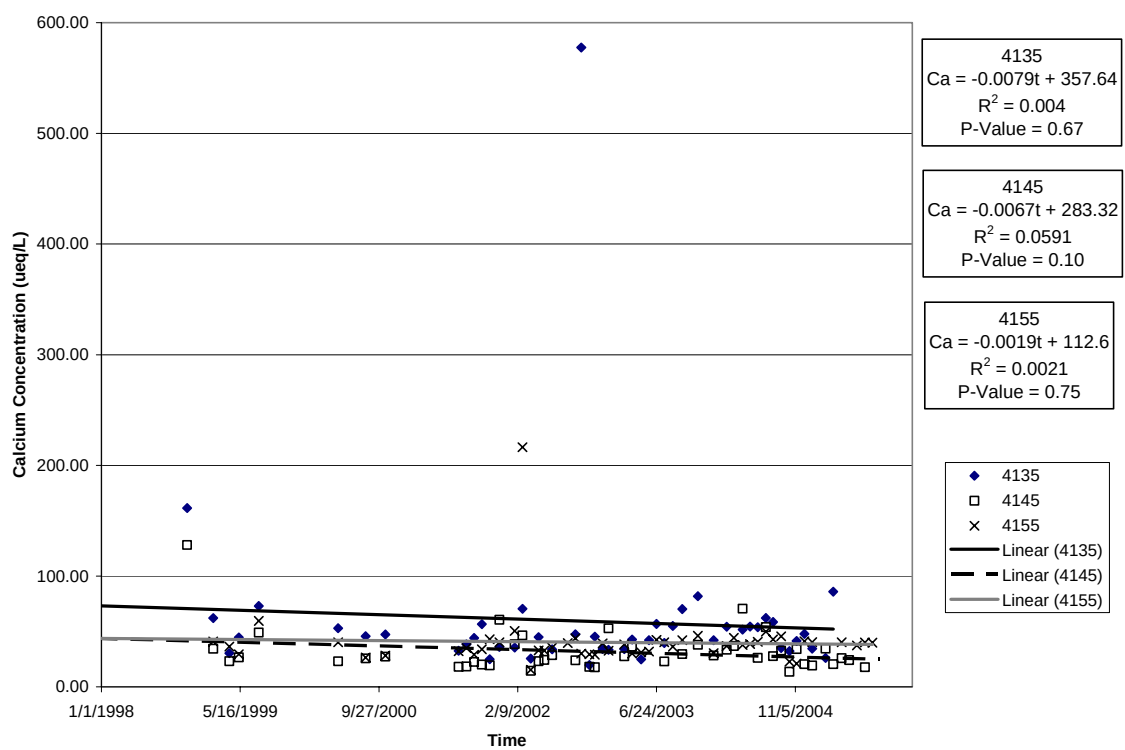


Figure 4. Calcium Concentration vs. Time for Noland Divide lysimeter data

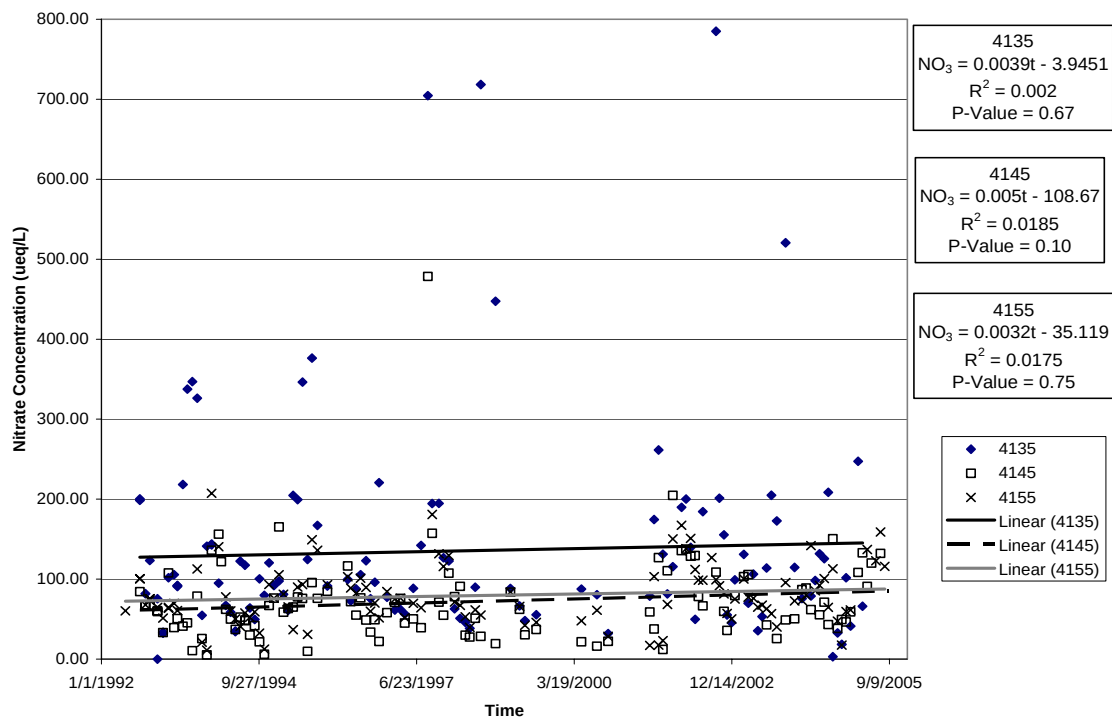


Figure 5. Nitrate Concentration vs. Time for Noland Divide lysimeter data

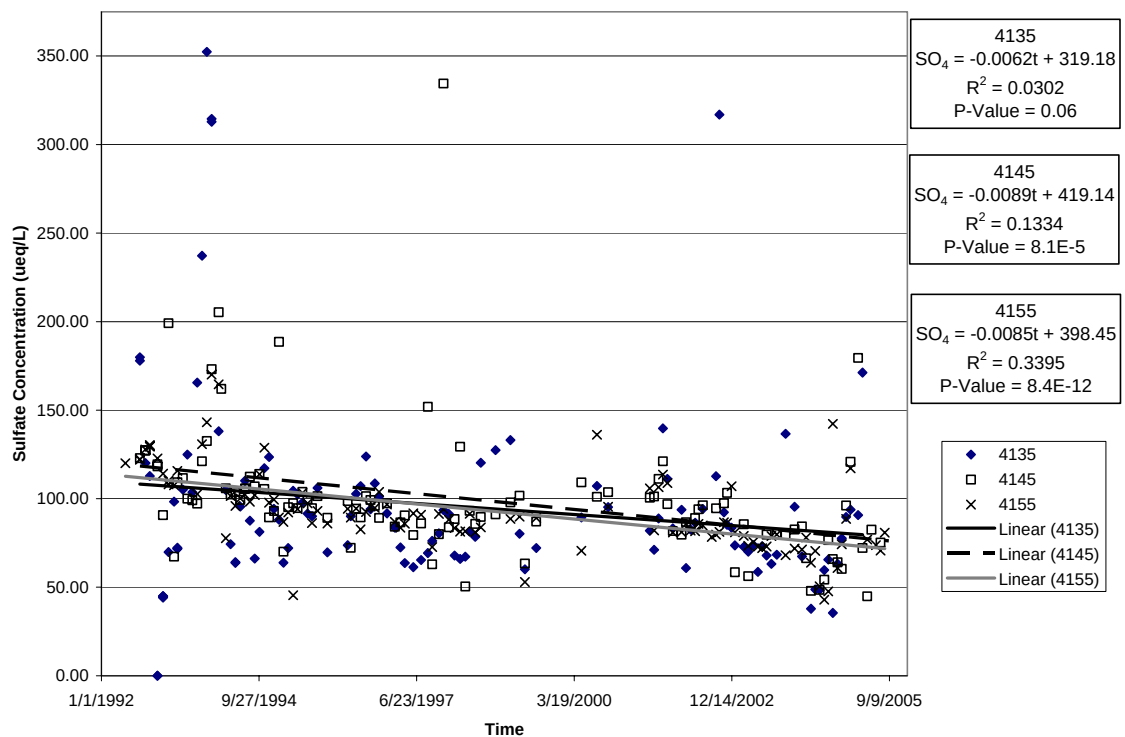


Figure 6. Sulfate Concentration vs. Time for Noland Divide lysimeter data

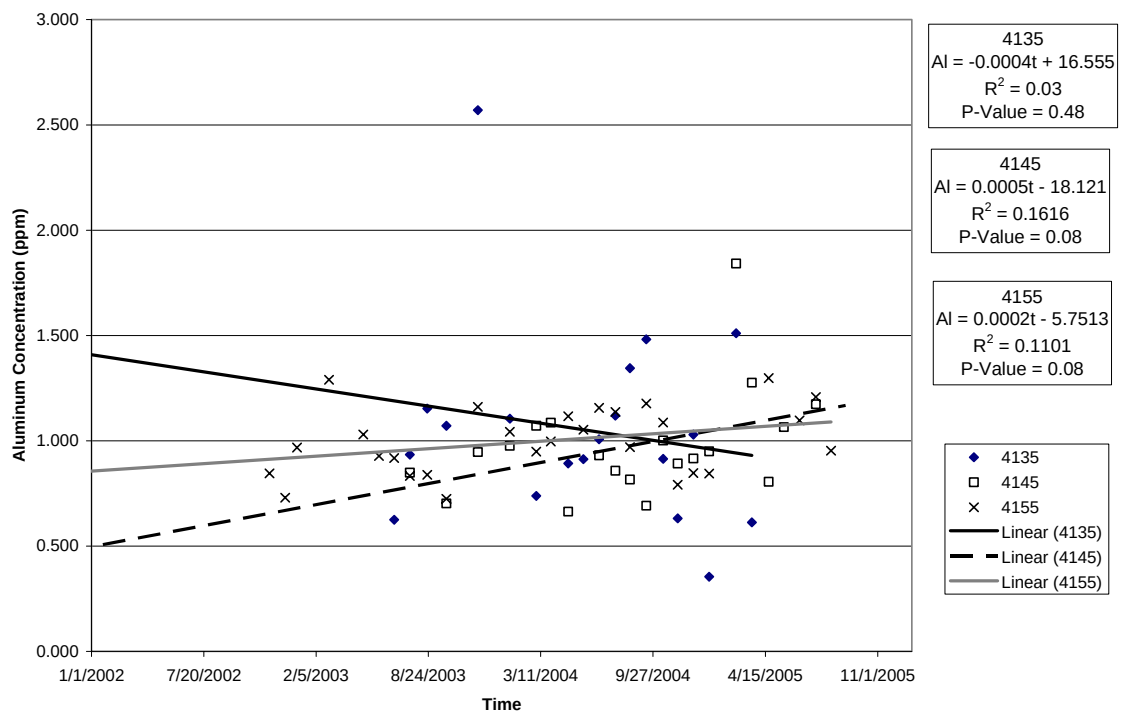


Figure 7. Aluminum Concentration vs. Time for Noland Divide lysimeter data

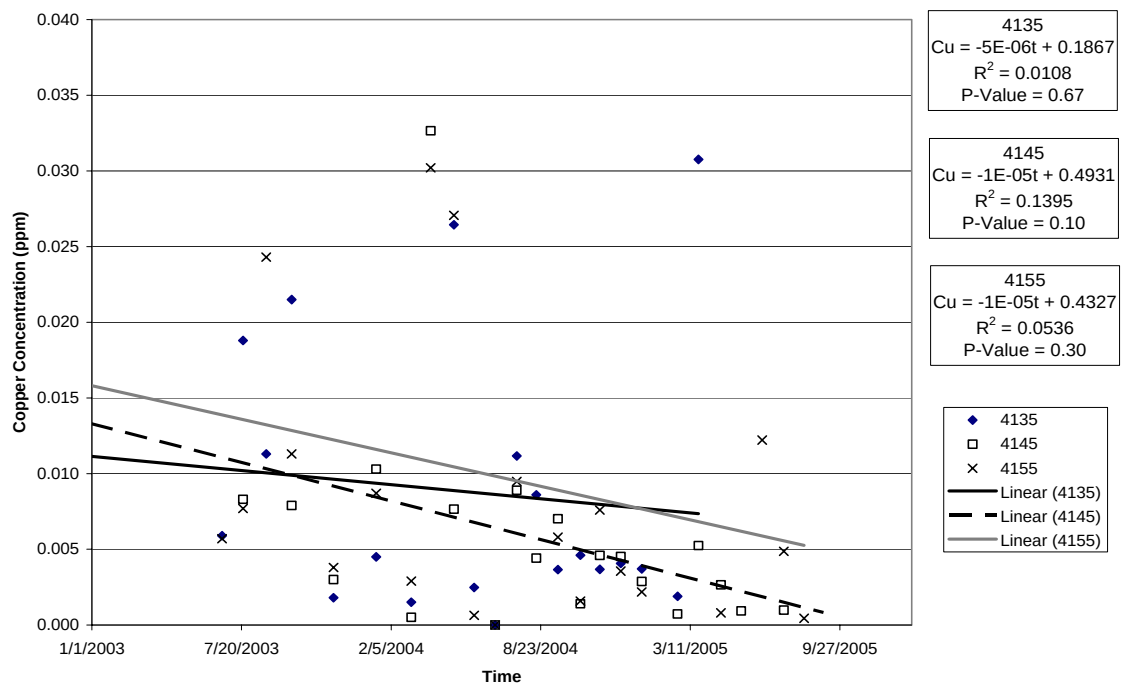


Figure 8. Copper Concentration vs. Time for Noland Divide lysimeter data

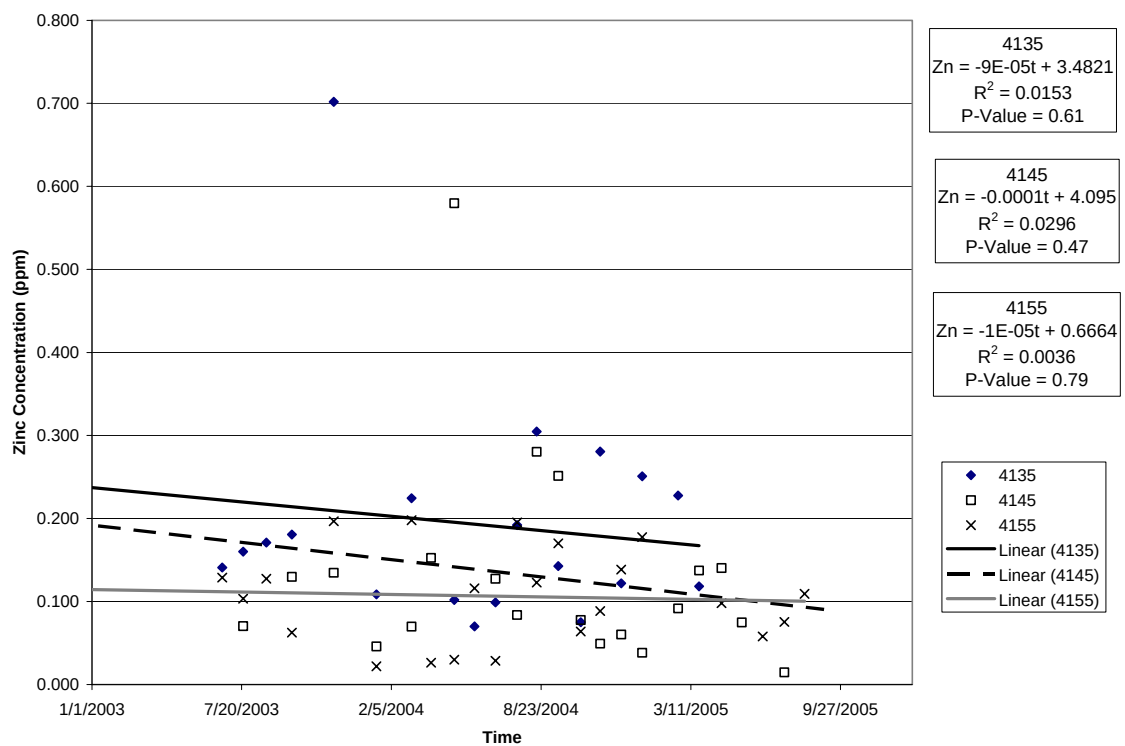


Figure 9. Zinc Concentration vs. Time for Noland Divide lysimeter data