To the Graduate Council:

I am submitting herewith a thesis written by Candice Ann Owen entitled “Using Multivariate Analysis of Geochemical Data to Better Define Hydrologic Interfaces in Surface Water - Groundwater Systems.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

_____
Randall Gentry, Major Professor

We have read this thesis
and recommend its acceptance:

Chris Cox
_____

John Schwartz
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Accepted for the Council:

_____
Carolyn R. Hodges,Vice Provost
and Dean of the Graduate School

(Originial signatures are on file with official student records.)

Using Multivariate Analysis of Geochemical Data to Better Define Hydrologic Interfaces in Surface Water - Groundwater Systems

A Thesis Presented for
the Master of Science
Degree
The University of Tennessee, Knoxville

Candice Ann Owen
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I would like to thank my parents for always believing I could do whatever I set my mind to and for teaching me the importance of character and respect for the beauty of nature all around me that has led me down this path. I would like to thank my siblings, Casey and Caroline, for laughing and crying with me and for always being there even when they wanted to kill me. I want to thank my grandparents, JC and Charlotte, for being two of my biggest fans, also my advisor, Dr Gentry for his help and guidance and for his friendship. Kiel Neff, Mei Ciao, and Edwin Deyton, I would like to acknowledge for all of their help with lab work, etc. and also Amanda McKenna for all of her collaboration on fieldwork and for being my sounding board. Finally, I want to thank my friends for their love and support and for the good times these past 6.5 years.

ABSTRACT

Groundwater-surface water interactions have been shown to be important to flow generation and stream chemistry in upland catchment environments. These areas, however, are often difficult to access making the implementation of standard hydrological surface and subsurface monitoring equipment and characterization procedures impractical, arduous and in many cases impossible due to the nature of the terrain and also regulatory guidelines for protected areas. By collecting surface water samples at distinct water contribution sites to a headwater stream, areas of groundwater influence were inferred and a hydrochemical conceptual model of a small basin was created.

The objectives of this research were to 1) understand the groundwater chemistry influences to an upland stream in the Great Smoky Mountains National Park (GSMNP) using limited surface water data 2) determine if the use of multivariate statistics could help delineate water interaction “types” within the study basin, 3) create a conceptual model to define the chemical interactions in the stream using a comparison of data. The objectives were met by the analyses of field data collected within Ramsey Prong, a remote forested, high elevation stream in the Middle Prong Little Pigeon River Watershed chosen for the study site. Eight sampling sites were selected at hydrologic and hydrochemically significant points in the basin. Three data collection trips were performed in April, July, and August of 2007. Water sampled for analysis of cations, anions, and trace metals was collected and flow measurements were recorded on each trip at each site.

Multivariate analyses were conducted on the collected data to detect correlations between parameters that might indicate similar chemistries or water interaction “types” where high correlations were displayed. Three water types: 1) surface water; 2) spring water; and 3) a top of catchment mixture of spring and highly acidic deposition and drainage water were delineated. Spring 1, located at the bottom of the study area, was designated as the first water type and

displayed high concentrations of Si, Na, ANC, and pH. The source of this water was affirmed by groundw32ater characteristics caused by the sandstone subsurface environment. The second water type, consisting of the two highest elevation sample sites, displayed characteristics of acid deposition and acid-rock or acid induced leaching including, low pH and ANC and high levels of SO_4, Mn, Fe, and Al ions. Increased levels of Si and Na also suggested groundwater interaction further up the sampled tributary. Water designated as the third water type consisted of the remaining in-stream samples which demonstrated a trend of general dilution in most atmospherically input ions and a concentrating of geochemical parameters. Large areas of focused recharge signatures were not detected in the study area leading to the assumption of primarily diffuse recharge throughout the stream. Two tributaries sampled on the August collection date displayed groundwater chemistries with a different signature than that of the stream and showed indications of water quality buffering. The analysis demonstrated the possibility for influential stream buffering in the GSMNP by groundwater and groundwater sourced inputs and also the importance of groundwater in this system.

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INTRODUCTION

Baseflow monitoring in a remote area can provide insights into the overall behavior and source characteristics of the local groundwater system. These groundwater-surface water behavior characteristics can also have a strong impact on the water quality and buffering that occurs during storm events and during extended baseflow periods. Groundwater-surface water interactions have been examined for a number of years and are recognized as having significant influences on stream environments (Sophocleous 2002). Groundwater in upland catchments has been shown to be the major component of surface flow during baseflow while buffering streams during high flow periods (Soulsby et al., 1998). Baseflow studies provide the opportunity to look at groundwater influxes when predominantly stable chemical and hydrologic factors are affecting the stream (Gburek and Folmar 1999; Soulsby et al., 1998). Groundwater is contributed to streams by flow from springs and tributaries; and exfiltration through streambeds and banks. Flow into a stream most likely occurs along the entire length of the stream**,** meaning subsurface flow is derived from throughout the watershed (Winter 2007; Shand et al., 2005). Many elements influence the discharge of groundwater to streams including topography, underlying geology and steam bed shape, subsurface hydraulic properties, stream stage, temporal variations in precipitation, and local groundwater flow patterns (Cey et al., 1998; Sophocleous 2002).

Diffuse and focused recharge are the two main catagories of subsurface flow into streams (National Research Council 2004b). Focused recharge in a hillslope environment is generally the effect of fractured rock environments and is associated with long water residence times due to connectivity with the geological system. Diffuse recharge in this setting is linked with flow through shallow drift and soils and is associated with short residence times and more uniform flow being mainly supplied by precipitation infiltration (Oxtobee et al. 2002; National Research Council 2004b). One type of recharge generally

dominates; however, both may be important to the system, in particular at the regional scale (Izbicki et al. 2002).

A recurring basic assumption of many hydrogeological studies in catchment settings dictates that factors such as source, pathway, and residence times exert strong influence on water chemistry.(Kendall and McDonnell 1998) Water-rock interactions with heterogeneous lithology and soil types have been found to be a major source of differing signatures in groundwater contributions (Negrel et al., 2003; Negrel et al., 2000; Sultan 2003; Soulsby et al., 1998). When geology and soil are relatively homogeneous variability in water quality may be assumed to arise from the length and type of interactions with the subsurface environment. It is well documented that residence times for groundwater dictate the degree of chemical transformation that occurs through processes such as absorption, oxidation, reduction, dissolution, and cation exchange (Kendall and McDonnell 1998). Flow paths also affect signatures by altering the conditions to which the water is exposed (Haria and Shand 2004). Unique chemistries in groundwater that arise from geology, residence times, and flow paths may allow for classification of the water into “types”. (Shand et al., 2005; Stutter et al., 2006) Examining the chemical make up of these water signatures may help to define the water-rock interactions conceptual model and the nature of flow patterns in the source area. The hydrogeochemistry of varying groundwater inputs into the stream from tributaries and springs has been examined in an attempt to identify water types and their interactions with the stream as well as to characterize the surface and subsurface environments in numerous studies (Negrel and Lachassagne 2000; Stutter et al., 2005**;** Genereux et al., 2001; Sultan 2003; Shand et al., 2005; Soulsby et al., 1998; Haria and Shand 2004; Soulsby et al. 1999).

The purpose of this study was to determine if water type characteristics could be developed by sampling surface water at baseflow along the main channel of a stream. The following objectives were formulated and met by the analyses of field data collected within a remote area of the Great Smoky

Mountains National Park: 1) develop an understanding of the groundwater chemistry influences to an upland stream in GSMNP using limited surface water data 2) determine if the use of multivariate statistics could help delineate water interaction “types” within the study basin, 3) create a conceptual model to define the chemical interactions in the stream using a comparison of data.

METHODS

Study Area:

The Great Smoky Mountains, a range of the Blue Ridge Mountains bordering between Tennessee and North Carolina, make up a southern portion of the Appalachian Mountain range running along the eastern side of the United States. The GSMNP normally has very high humidity and precipitation, averaging from 1.4 m (55 in.) per year in the valleys to 2.2 m (85 in.) per year on the peaks. Vegetation in the park includes a plethora of biota, with forests ranging from the deciduous Cove Hardwood at lower elevations to the boreal Spruce-Fir, at higher elevations. Temperatures in the Smokies vary considerably with season but display an annual average daily high of 21.4°C (70.5 °F) and a daily low of 6.3°C (43.3 °F) in the lower areas of the park and an annual average daily high of 9.9°C (49.9°F) and a daily low of 1.9°C (35.5°F) in the highest elevation areas (National Park Service).

The study area is a part of the Middle Prong Little Pigeon River Watershed located in the Greenbrier Valley in the northeastern section of the park near the town of Gatlinburg, Tennessee. In the small basin-sized area (roughly 10 square kilometers) chosen for this study Ramsey Prong, a small headwater stream, flows down through the watershed and converges with Middle Prong (Figure 1.). This site was chosen to be evaluated due in part to its accessibility along the Ramsey Cascade Trail and also its location in relation to fish monitoring and water quality studies being conducted on the Middle and Ramsey Prongs of the watershed thus, providing the opportunity for future correlation between groundwater-surface water interactions and spatial patterns in brook trout.

The geology of the study basin is mainly Thunderhead sandstone; a thick-bedded sandstone primarily composed of quartz and potassic feldspar grains with a lesser quantity of plagioclase feldspar (King et al. 1968). This lithology is assumed to be relatively homogeneous throughout the study area. Soil types

within the area include Ditney, a dark yellowish brown loam, and Unico, a dark yellowish brown channery loam that are described as shallow, excessively drained, with moderately rapid permeability (Natural Water Resources Conservation Service).

Stream acidification has been documented in the Appalachian Mountains for a number of years (Herlihy et al., 1993) and is associated with low pH and ANC values in areas of noncarbonated sedimentary bedrock, high elevation, steep slopes, base poor soils, and high precipitation (Sullivan et al., 2007). Two major causes of stream acidification are acid deposition and acid rock drainage both of which have been documented in the GSMNP (Herlithy et al., 1991; Hammatstrom et al., 2003; Huckabee et al., 1975). Acid deposition from precipitation and fog or clouds has been associated with low pH and ANC and heightened levels of SO_4, and NO_3 in stream waters of the GSMNP (Cook et al., 1994). Acid rock drainage is caused by the weathering of sulfide minerals and is possible in the study area due to Anakeesta geology containing the disseminated iron sulfide minerals, pyrite and pyrrhotite (Huckabee et al., 1975). The reduced iron and sulfur are oxidized by natural processes to produce H^+, $Fe(OH)_3$ and SO_4. These ions are then hydraulically transported to streams where they cause acidification. Secondary minerals temporarily sequester Fe and other metal ions and storm events cause their dissolution leading to poor water quality during storm events. Fe, Al, Mg, and Mn are the major constituents of the secondary minerals found forming on pyritic rocks in the region of the study area (Hammerstrom et al., 2003). Acid mine drainage which involves the anthropogenic exposure of minerals to the elements would be expected to cause the same affects but has not been documented in the study area, however, acid rock drainage has been shown to occur in areas with no anthropocentric influences and therefore maybe occurring in the study basin (Huckabee et al., 1975). Due to the nature of the study, delineating between the acid rain influence of mineral leaching in the rocks of the area and

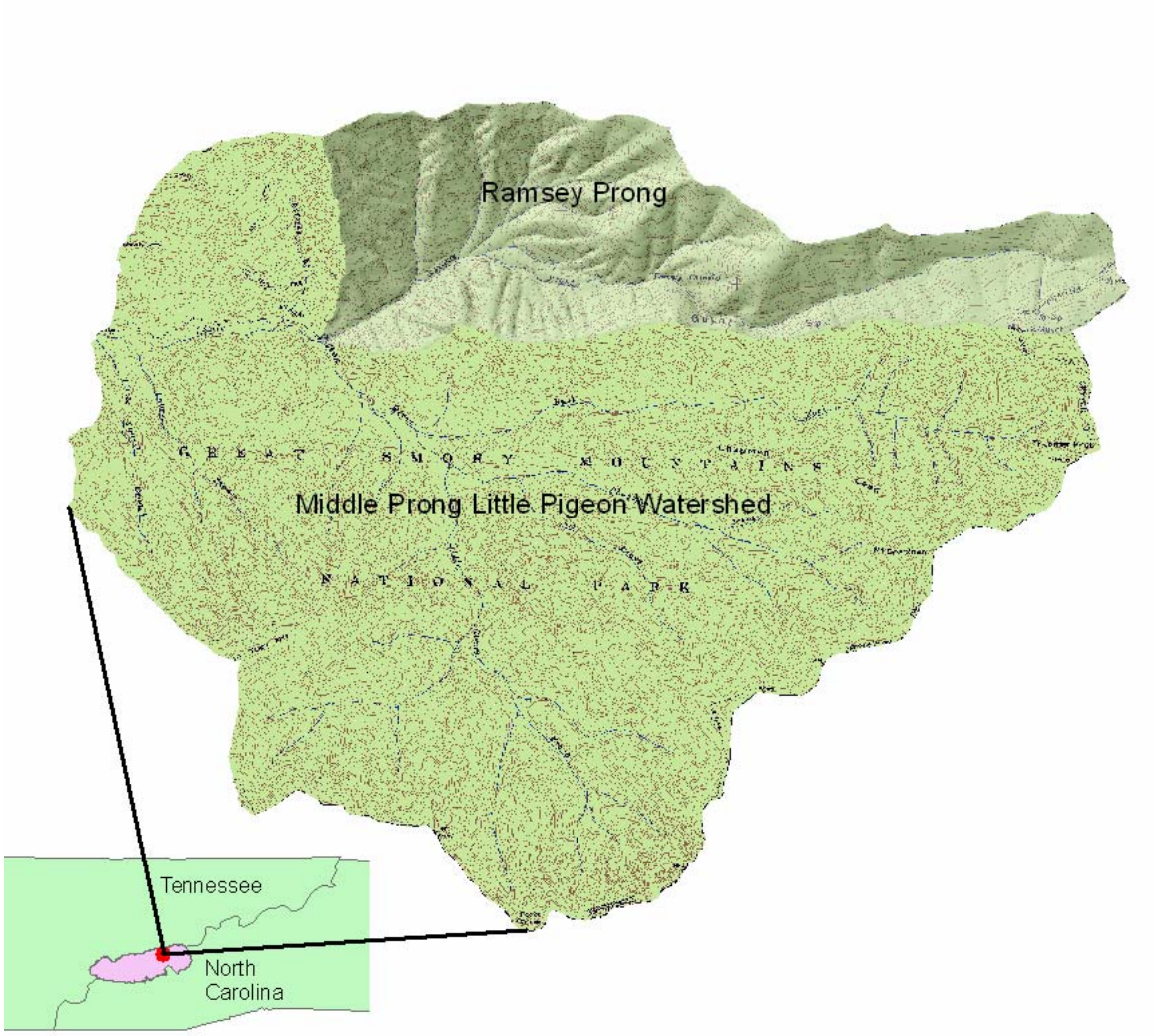

Figure 1. Location of Ramsey Prong within the Middle Prong Little Pigeon Watershed and GSMNP.

the actual weathering of Anakeesta rock is not possible, however the baseflow conditions of the study suggest a possible combination of both.

Study Design:

Sampling locations, shown in Figure 2, were placed in the vicinity of accessible tributaries and a spring flowing into the prong where assumed groundwater and surface flow were contributing to the stream from higher elevation areas of the basin. Samples from six in stream sites were collected for all three dates. Locations included directly below Ramsey Cascade at the top of the study area and directly before the convergence of Ramsey Prong with Middle Prong at the bottom of the study area. Sites were also located directly above and below the lower two tributaries. The final two sites were chosen due to potential for significant chemistry influences. These included a spring, located on the trail, between Sites 6 and 7 which appeared to be a significant point groundwater recharge, and also a tributary at the top of the watershed suspected of being influenced by acid-rock drainage. Sampling of the remaining two tributaries in the study area was conducted on only the August date. The locations of tributaries flowing into the Ramsey Prong were determined using USGS map data and site reconnaissance. 500 mL water samples were collected for analysis of major and trace ions by first rinsing the bottle three times and then submerging the bottle midstream. On-site pH, conductivity, dissolved oxygen, and temperature were measured using a portable YSI 556 MSP Hydrolab. The Hydrolab was calibrated prior to each sampling event to ensure measurement accuracy and consistency, however, erratic behavior of the Hydrolab while in the field led to the use of lab analysis for pH and Conductivity. Cross-sectional flows at each in stream site were determined by measuring velocity using a Flowmate Model 2000 Portable Flowmeter as reported in (McKenna 2007).

The collection times were at least 24-hours after a storm event of over 1 inch precipitation to ensure that samples were collected at or near baseflow conditions. The samples were collected on three occasions: once in April, July,

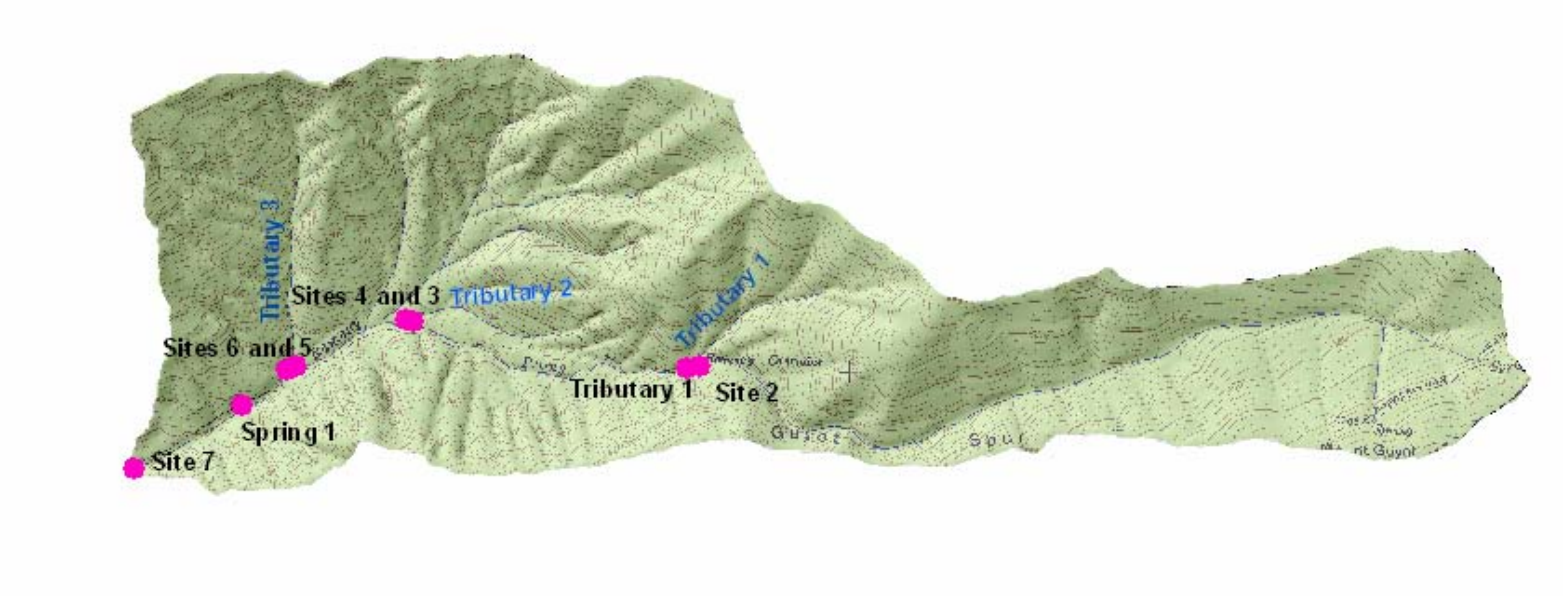

Figure 2. Site Locations on Ramsey Prong.

and August. All samples were collected LDPE plastic bottles triple rinsed with de-ionized water Sampling dates were initially designed to capture the two temporally extreme times of year, high and low flow, to afford a synoptic analysis of the area. Weather trends in the studied time period, however, did not follow normal seasonal patterns and were characterized regionally as severe drought during most of the study period. . Sampling was not possible for Sites 5 and 6 on the July date due to the onset of inclement weather. Spring 1 was flowing only in April preventing sampling for the last two collection dates.

Precipitation data for 2007 and also monthly and yearly averages were obtained for Gatlinburg, TN (Weather Underground). These measurements were compared with GSMNP data at the Park Headquarters and at Newfound Gap, shown in the Appendices. At the time of the first sampling, precipitation levels were around 484 mm (19 in.) below average rainfall levels to date for the year, in July levels were 928 mm (37 in.) below and in August 1044 mm (41 in.) below average to date for the year. The drought conditions confounded the interpretation of “normal” conditions in the study area. However, the lack of precipitation did lead to a purer groundwater signal, from baseflow, than may be present in non-drought periods.

Throughfall precipitation was collected monthly or after storm events in polyethylene buckets with eight-inch plastic funnels from two collection sites in the area. This precipitation data was used to make a qualitative comparison of stream chemistry to throughfall chemistries. One throughfall collection site was located on Ramsey Prong between Sites 6 and 7, while the other site was located on Eagle Rocks Prong at an elevation of 966 meters comparable to that of Ramsey Cascade (Site 2 and Tributary 1) at around 950 meters.

Analytical Procedures:

Major cations and trace metals Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, Al^{n+}, Cu, Fe, Mn, Si, Zn were measured for all samples using EPA Method 6010B & 6010C for a Thermo-Electron ® inductively coupled plasma (ICP) spectrometer. Major anions $NO_3^{2-}, SO_4^{2-}, Cl^-$ and NH_4^+ were measured using a Dionex ® ion chromatograph (IC). Acid Neutralization Capacity (ANC), pH, and conductivity were measured using a ManTech ®autotitrator following EPA Method 150.1, EPA Method 120.1, and Automated Gran Titration for low ionic strength waters as in Hillman et al. (1986), respectively.

Quality Control and Assurance (QA/QC) for chemical analyses were maintained by a number of methods. Samples were refrigerated immediately upon return from the field. ANC was analyzed within 24 hours of collection. Ion balances were performed on samples for additional quality assurance and samples were reanalyzed when a below 15% difference was not achieved. The study samples were analyzed as a subset of a larger set of samples and were included in those QA/QC practices. For the IC, QA/QC included reagent blanks (5%), spikes (5%), and replicates (10%). The QA/QC was checked by the parameters of accuracy and repeatability. One known USGS solution was run with 10% of samples as a check for accuracy while remeasuring samples served as a check for repeatability, 5% per batch. Detection limit was obtained by measuring a diluted standard solution diluted by two or five times until no data could be read from the peak. The smallest concentration is the detection limit. This method is appropriate if there is no peak for blank solution. Otherwise, the method from IUPAC is employed to determine detection limit by measuring blank sample for 10 times to calculate by using following equation: Detection Limit = blank sample mean + 3 × standard deviation.

Quality control for the ICP included a QCC sample being ran ever 12 samples. The software was programmed to ensure the QCC sample gave concentrations within 10% of what was expected. If the concentration of a particular element was not within 10%, the element was flagged as a failure. A trace metal sample obtained from the USGS was run every 12 samples also. The most probable values for this sample was be obtained from the USGS's Standard Reference Sample website, which was then compared to the ICP results to ensure that results were within 10% of the most probable values. Once every 20 samples a split was prepared and compared to the original sample and these should have been within 15% of each other. Every 20 samples a spike was prepared. The result for the actual sample was then subtracted from the spike sample and divided by the actual amount of the spike to provide a percent recovery. The percent recovery should range from 85% to 115%. A blank prepared from de-ionized water and acidified to 1% with ultra pure nitric acid was ran once every 24 samples. The results were checked to ensure blank concentrations were near zero. Minimum detection limits are determined annually. The method to determine detection limits was as follows: a) run 7 replicates of blank samples twice on two separate days, b) determine the standard deviation for each metal from the 14 blank samples, c) multiply the standard deviation of each metal by 3, this is the minimum detection limit for each metal. The detection limits should be within a factor of 2 from the blue book value stated in Standard Methods for the Examination of Water and Wastewater.

Quality control for the Autotitrator included a number of procedures and a more thorough explanation of these and other analyses procedures is located in the Appendices.

Statistical Analysis:

The statistical program JMP version 6 was used to generate multivariate correlation matrices and corresponding bivariate combination plots. Ten physico-chemical constituents (pH, ANC, Ca^{2+}, Na^{+}, Mg^{2+}, Al^{n+}, Fe, Mn, Si, NO_3^{2-}, SO_4^{2-}) , were used in the analyses.

RESULTS AND DISCUSSION

Spatial Comparisons of Chemistry and Isotopic Signatures:

Physiochemical parameters collected for all sites and dates are summarized in Table 1. Table 2 is a summary of chemistry statistics and displays mean, standard deviation, and maximum and minimum values for the parameters. Comparing values provided the ability to identify and understand how different spatial factors affected watershed wide chemistry. Plots of major parameters with site for the three collection dates are shown in Figures 3-13. These parameters generally displayed a recognizable trend moving down from the headwaters. Ions suspected of being caused by acid deposition or acid-rock drainage/acid deposition leaching contributions (NO_3^{2-}, SO_4^{2-} , Cl, Al, Fe, Mn, Zn) generally decreased in concentration with decreases in elevation. This can be attributed to dilution by groundwater inputs, as can upward trends in pH and ANC. Most of the ions not suspected of being caused by acid contributing sources (Na, Ca, Mg, K, and Si) increased or remained relatively constant in concentration with distance from headwaters, representing a steady input along individual reaches throughout the system.

Examining the site samples for water type characterization resulted in two additional signatures from that of the general stream water quality (Table 3.). These water types were located at sites near the top, Tributary 1 and Site 2, and bottom, Spring 1, of the study area. Tributary 1, located directly below the cascade, displayed pH and ANC values that were slightly lower than those of Site 2 located in the near vicinity (Figures 3 and 4.). Higher relative concentrations of Fe, Mn, Al, and SO_4 suggest influences of acid rain dissolution influences or acid-rock drainage from Anakeesta geology (Figures 6 and 10-12.). This was also supported by the occurrence of a yellowish-brown coloration on the tributary bed and in the water assumed to be the precipitate $Fe(OH)_3$. Decreases in the

Table 1. Chemical data for all sites and collection dates and comparison throughfall chemistries.

Sample	Sampling Date	pH	ANC	Conductivity	Dissolved Ions (mg/L)								
			(µeq/L)	(µs/cm)	NO3	SO4	Na	Mg	Ca	Al	Mn	Si	Fe
Site 2	April	4.366	-10.360	15.950	3.4961	1.9961	0.594	0.232	0.865	0.166	0.019	1.808	BDL
	July	4.882	-10.610	16.880	2.602	2.556	0.579	0.237	0.851	0.192	0.021	1.858	0.025
	August	4.991	-13.723	14.470	2.2627	2.1106	0.727	0.202	0.695	0.124	0.016	1.906	0.016
Tributary 1	April	4.234	-3.084	21.300	3.5314	2.4616	0.613	0.253	0.907	0.227	0.031	2.316	0.017
	July	4.711	-22.760	18.480	1.080	2.877	0.686	0.186	0.558	0.266	0.023	2.561	0.072
	August	4.686	-21.084	18.960	1.0761	2.8676	0.635	0.185	0.626	0.273	0.020	2.609	0.088
Site 3	April	4.557	-11.084	15.370	3.3428	1.9377	0.612	0.244	0.922	0.121	0.017	2.020	BDL
	July	5.034	-10.174	15.880	2.173	2.409	0.594	0.231	0.758	0.170	0.019	1.841	0.025
	August	5.151	-4.108	13.800	1.9184	2.0801	0.615	0.192	0.705	0.106	0.016	2.144	0.014
Site 4	April	4.666	-6.842	15.140	3.3808	1.9146	0.653	0.245	0.949	0.108	0.016	2.039	BDL
	July	5.059	-6.940	15.550	2.077	2.411	0.611	0.233	0.874	0.180	0.021	1.876	0.023
	August	5.287	-3.269	13.250	1.8661	2.0296	0.647	0.198	0.681	0.107	0.016	2.189	0.013
Site 5	April	5.066	1.297	14.260	3.2755	1.8211	0.648	0.250	0.962	0.067	0.008	2.194	BDL
	August	5.621	-1.697	12.540	1.7268	1.9389	0.667	0.200	0.729	0.093	0.007	2.404	0.013
Site 6	April	5.228	2.555	13.550	2.8891	1.6980	0.636	0.236	0.898	0.059	0.008	2.237	BDL
	August	5.863	7.006	12.100	1.6196	1.8563	0.694	0.197	0.774	0.074	0.005	2.462	0.013
Spring 1	April	6.008	43.835	8.560	0.0578	0.7255	0.838	0.101	0.468	0.024	BDL	3.204	BDL
Site 7	April	5.272	3.295	13.410	2.7114	1.6591	0.648	0.236	0.922	0.051	0.003	2.304	BDL
	July	5.664	1.404	13.320	1.969	2.186	0.645	0.227	0.763	0.109	0.006	2.050	0.012
	August	5.879	9.567	12.100	1.5783	1.8508	0.672	0.194	0.722	0.084	BDL	2.491	0.017
Tributary 2	August	6.234	23.223	13.310	1.7063	1.5726	0.781	0.240	0.942	0.065	0.006	2.767	0.014
Tributary 3	August	6.507	41.269	10.510	0.7212	1.0805	0.723	0.181	0.665	0.030	BDL	2.839	0.013
Precipitation													
Eagle Rock	April	4.294	-5.797	17.000	1.188	2.935	0.200	0.128	0.660	0.034	0.075	0.039	0.015
Ramsey Prong	March	4.933	-0.547	19.690	0.266	3.292	0.374	0.284	1.141	0.078	0.057	BDL	0.015

Table 1. Chemistry Statistical Summary.

	pH	Conductivity	ANC	Cl	NO3	SO4	Na	NH4
		(µs/cm)	(µeq/L)	(mg/L)				
Mean	5.11	14.744	-2.839	0.383	2.231	2.069	0.651	0.006
Std Dev	0.51	2.800	13.868	0.574	0.932	0.474	0.057	0.001
Min	4.23	8.560	-22.760	0.292	0.058	0.726	0.579	0.003
Max	6.01	21.300	43.830	0.511	3.531	2.877	0.838	0.008

	K	Mg	Ca	Al	Fe	Mn	Si	Zn
	(mg/L)							
Mean	0.275	0.214	0.781	0.130	0.022	0.014	2.226	0.021
Std Dev	0.104	0.035	0.136	0.061	0.021	0.008	0.339	0.007
Min	0.165	0.101	0.486	0.024	0.012	0.002	1.808	0.009
Max	0.492	0.253	0.962	0.273	0.088	0.031	3.204	0.035

Table 2. Water Type Characterization.

Water Types	Characteristics	Chemistry	Location
Type 1	Acid Deposition/ Acid Rock Drainage	Lower pH and ANC High concentrations of SO_4, Al, Fe, and Mn	Site 2 and Tributary 1
Type 2	Groundwater Input	Higher pH, ANC, and Si Low SO_4, NO_3	Spring 1
Type 3	Muted Groundwater and Acid Input with Overall Spatial Trends	Trends of Increasing pH, ANC, and Si Trends of decreasing SO4, NO3 Al, Fe, and Mn	Sites 3-7

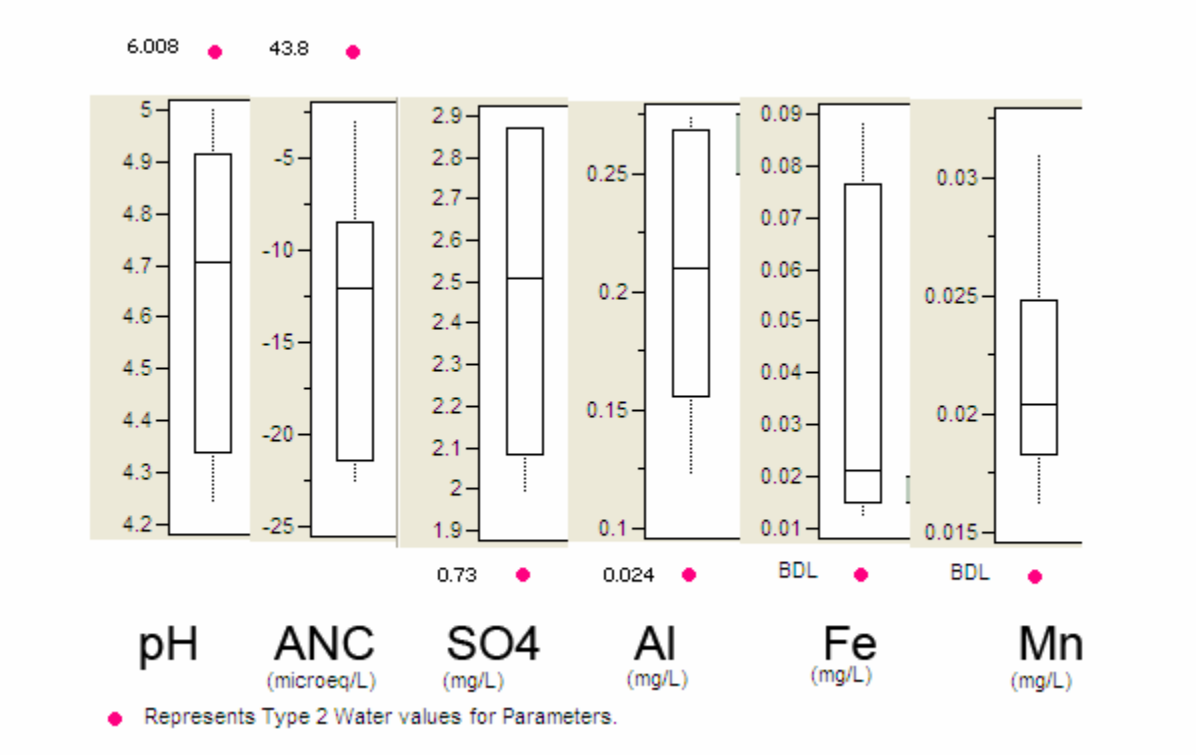

Figure 3. Box-Whisker plots for main ions of Type 1 water with values for Type 2 water shown.

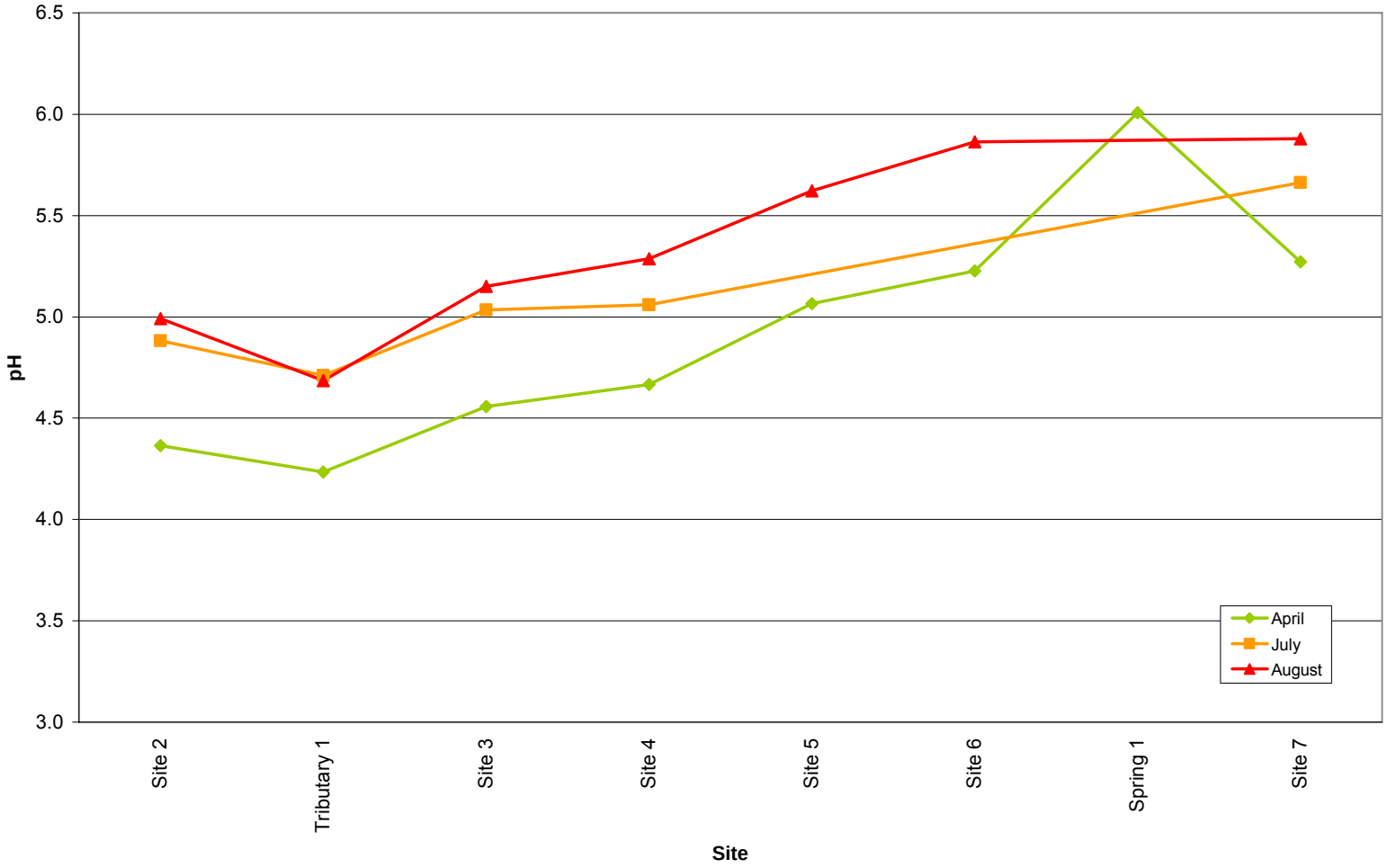

Figure 4. pH plotted against collection site.

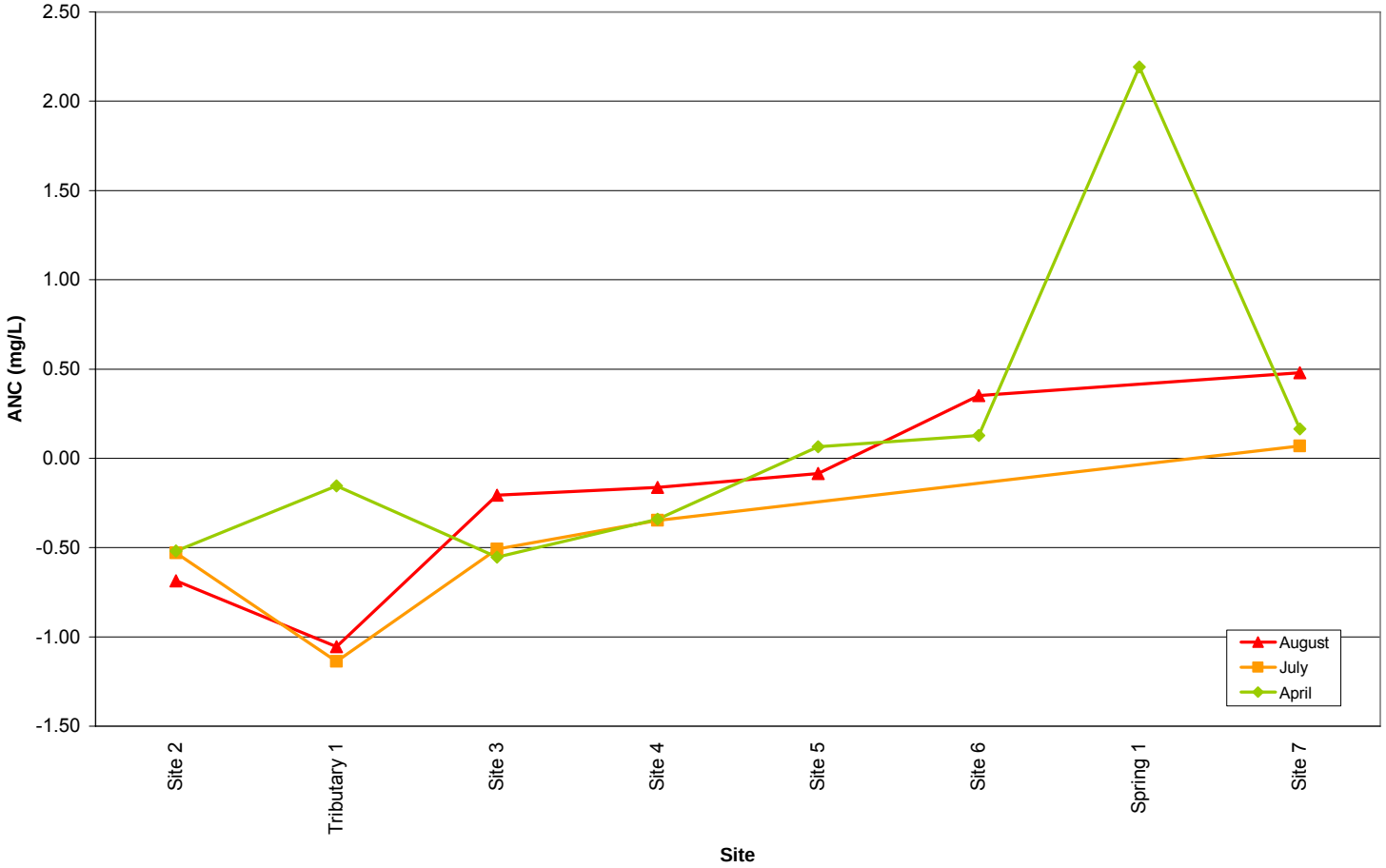

Figure 5. ANC plotted against collection site.

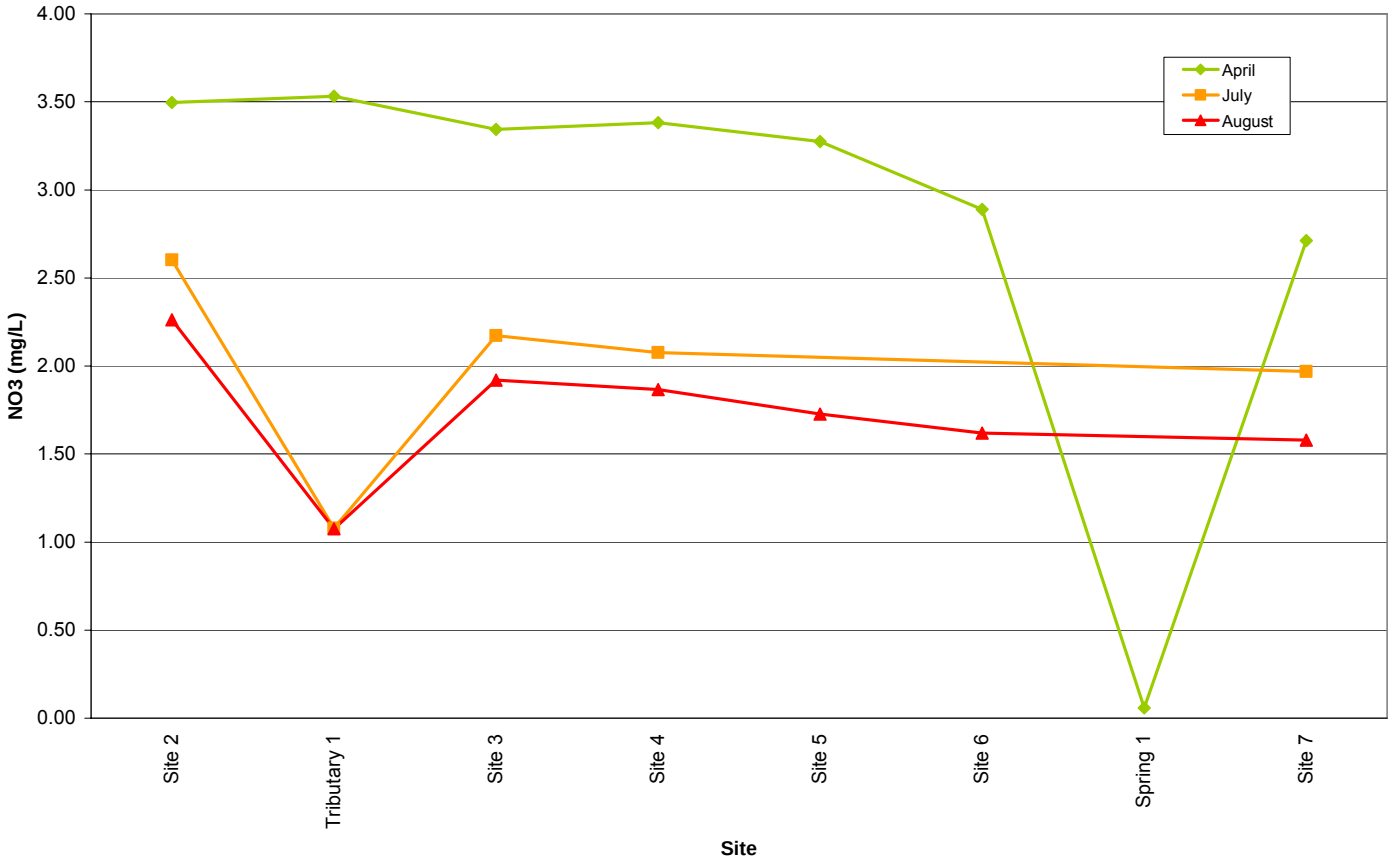

Figure 6. NO_3 plotted against collection site.

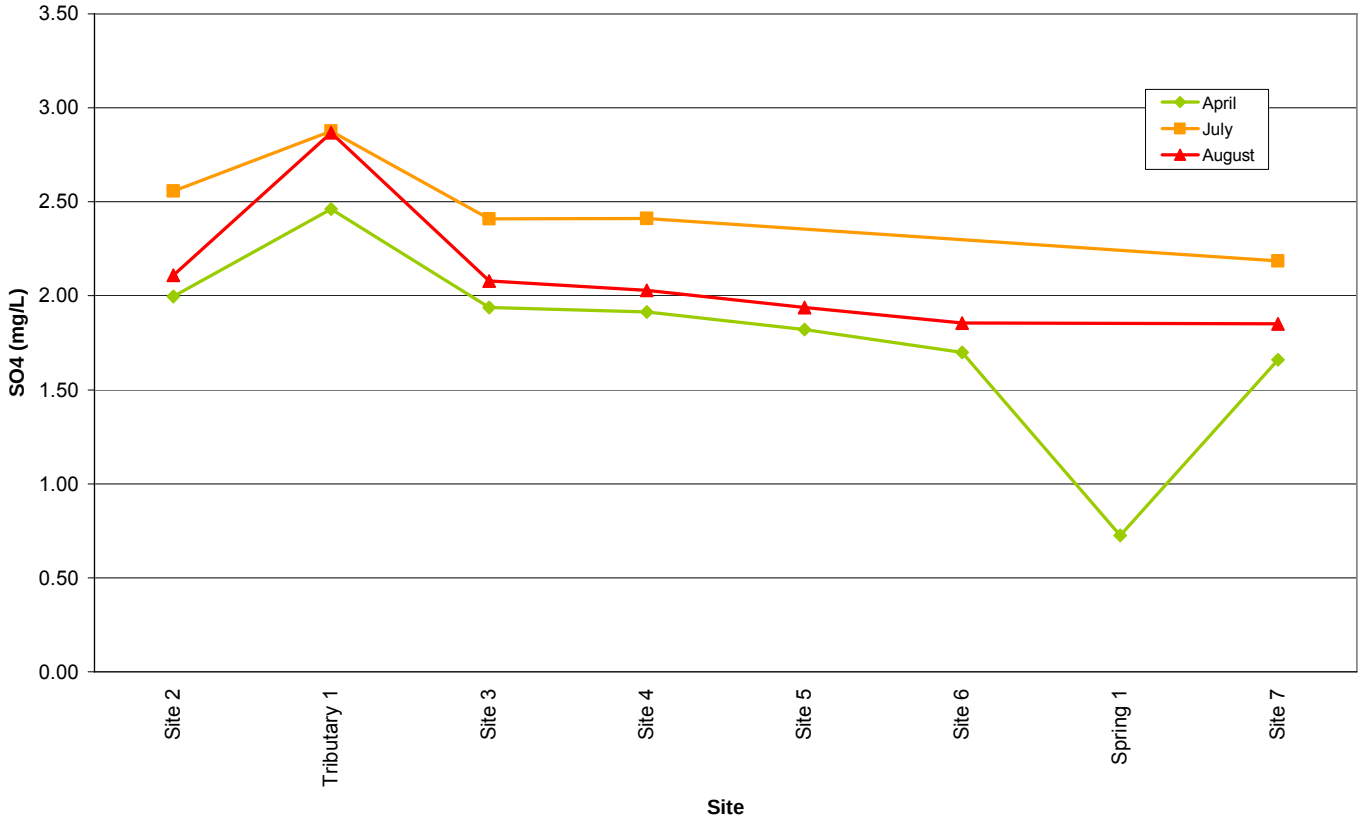

Figure 7. SO_4 plotted against collection site.

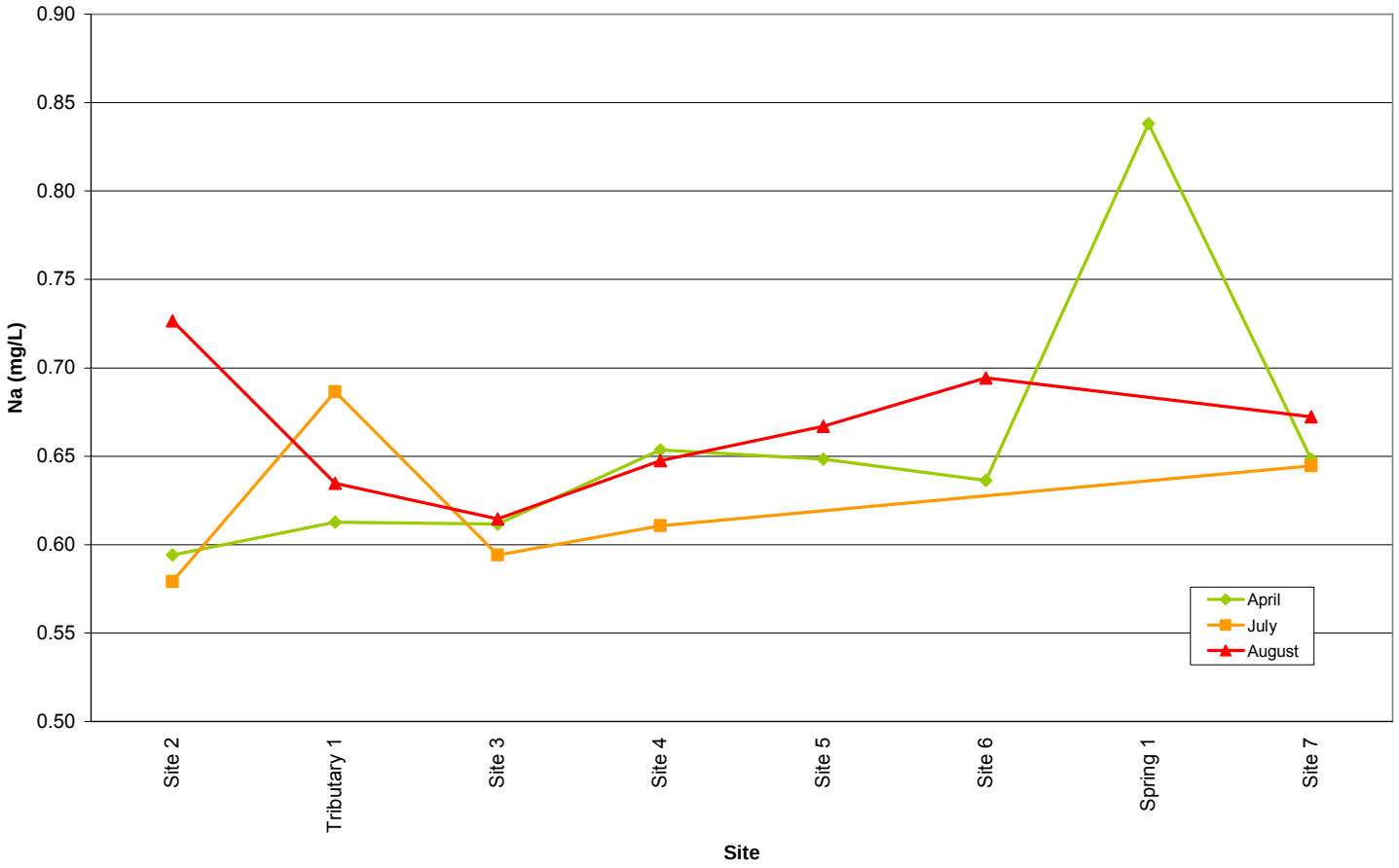

Figure 8. Na plotted against collection site.

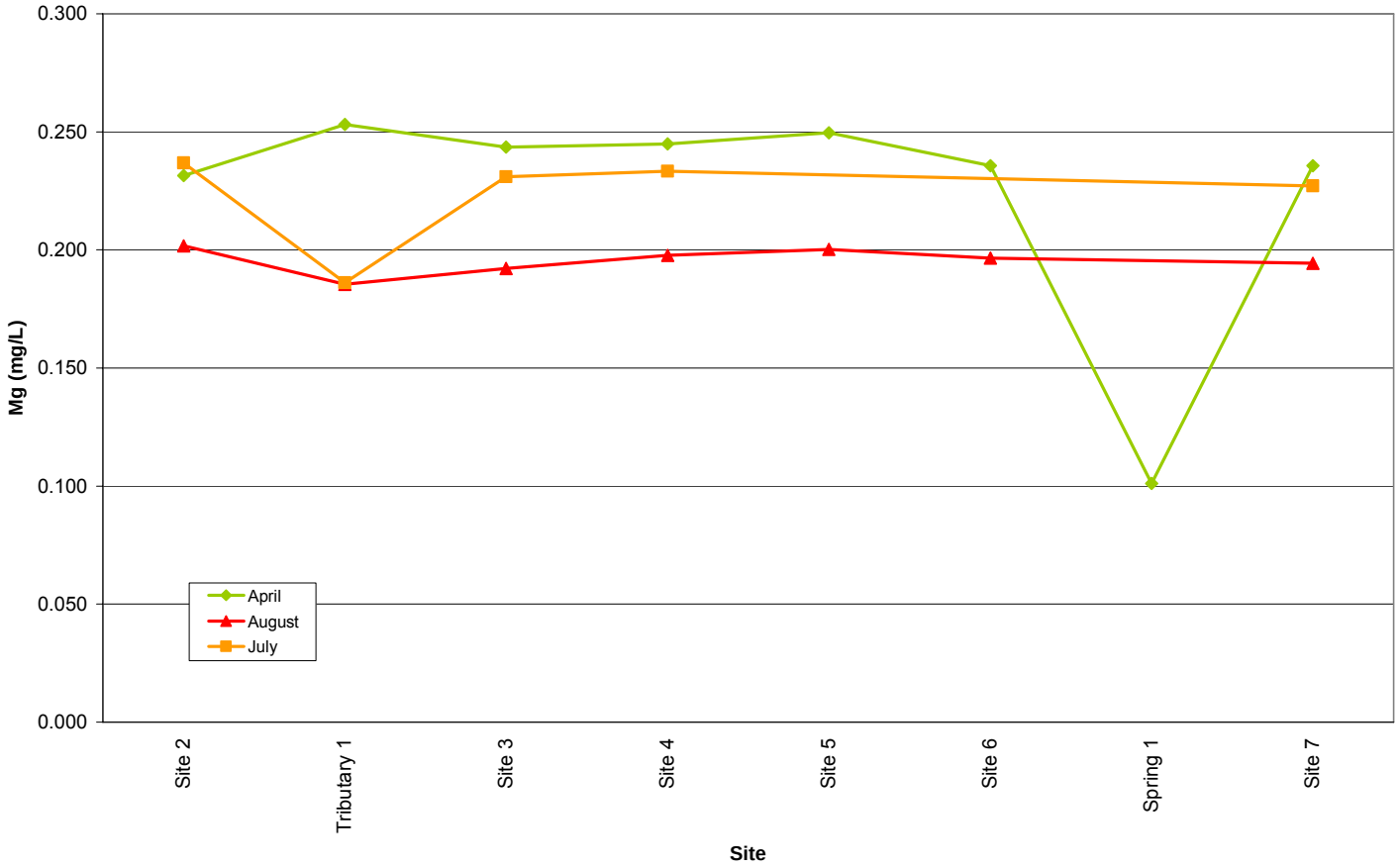

Figure 9. Mg plotted against collection date.

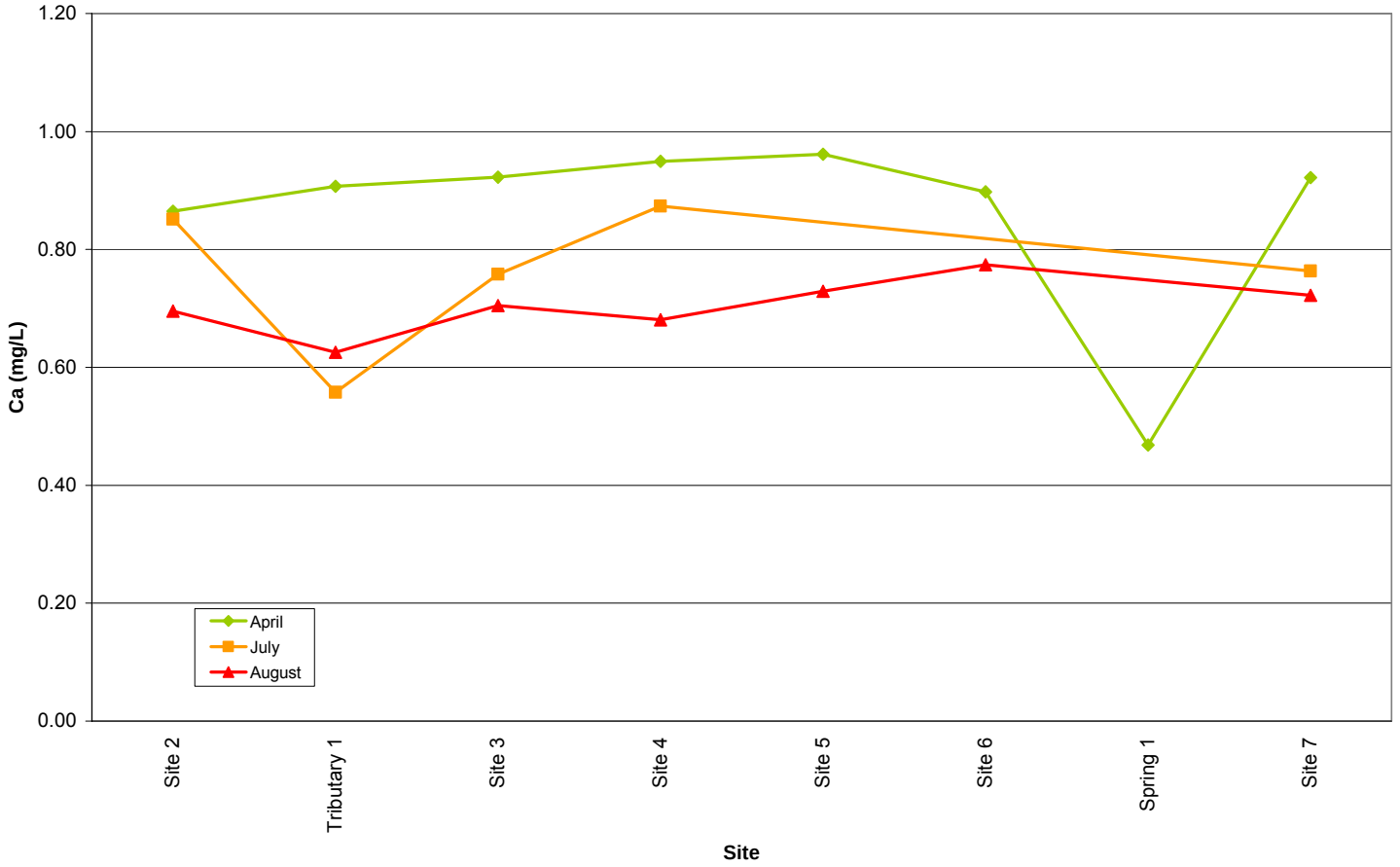

Figure 10. Ca plotted against collection site.

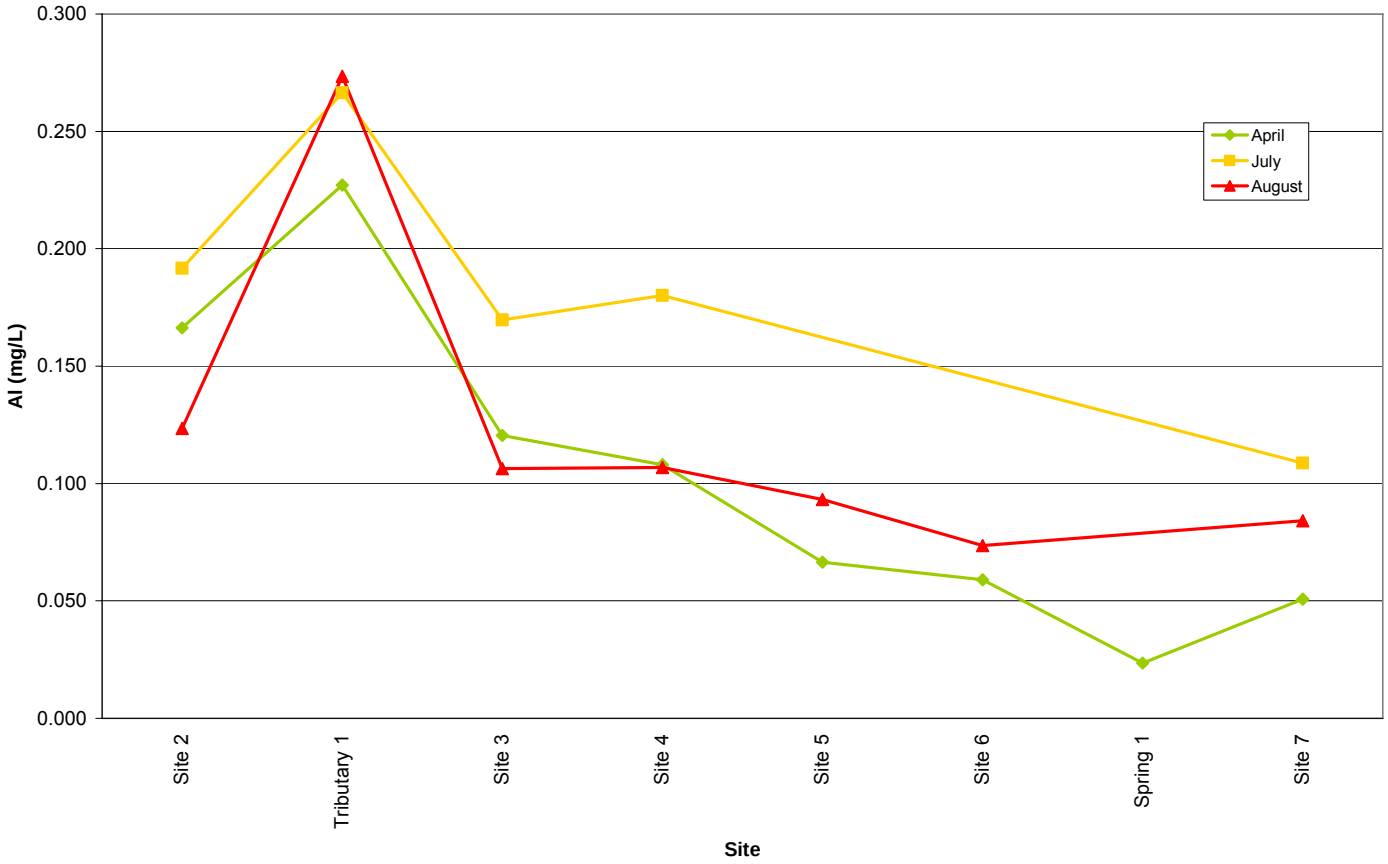

Figure 11. Al plotted against collection date.

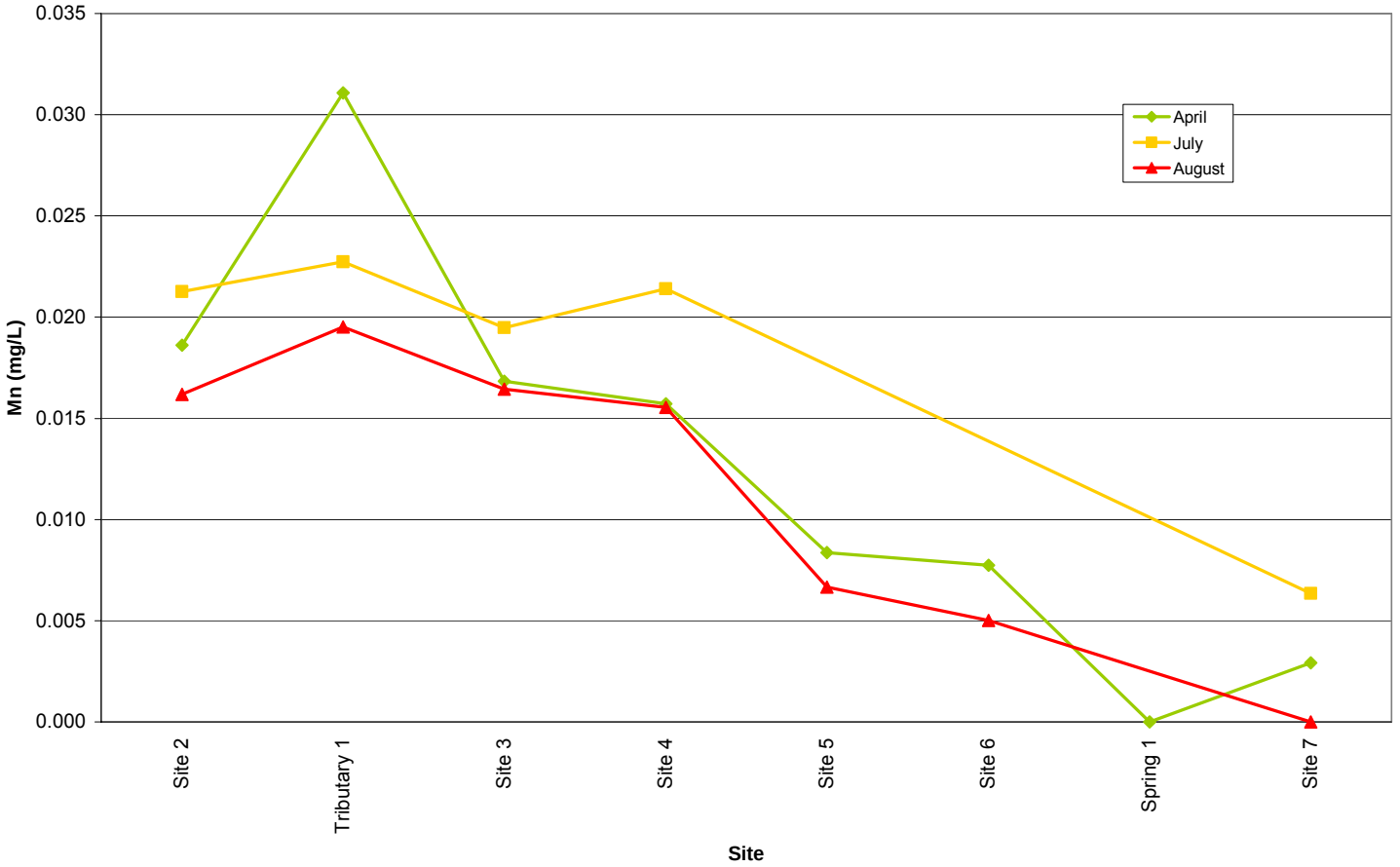

Figure 12. Mn plotted against collection date.

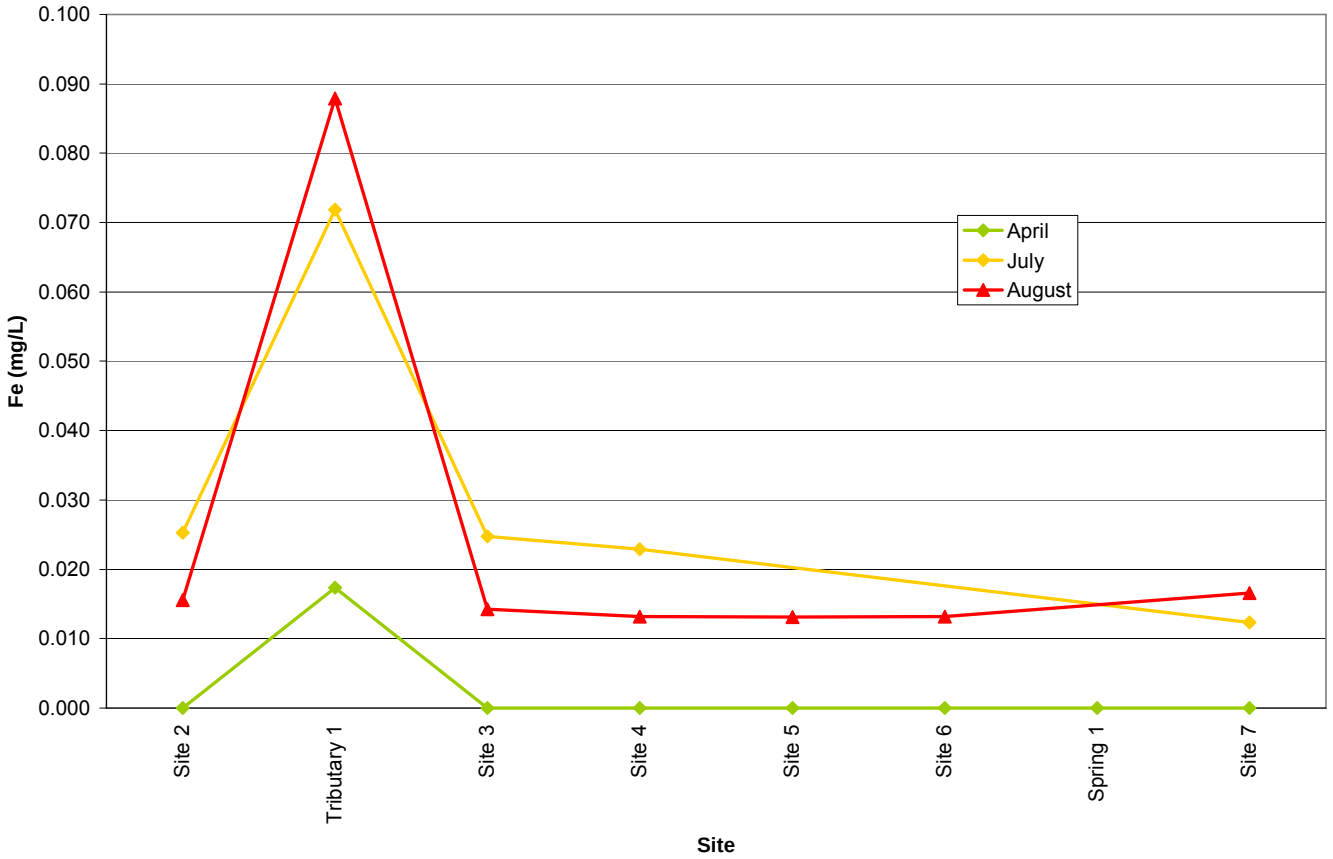

Figure 13. Fe plotted against collection date.

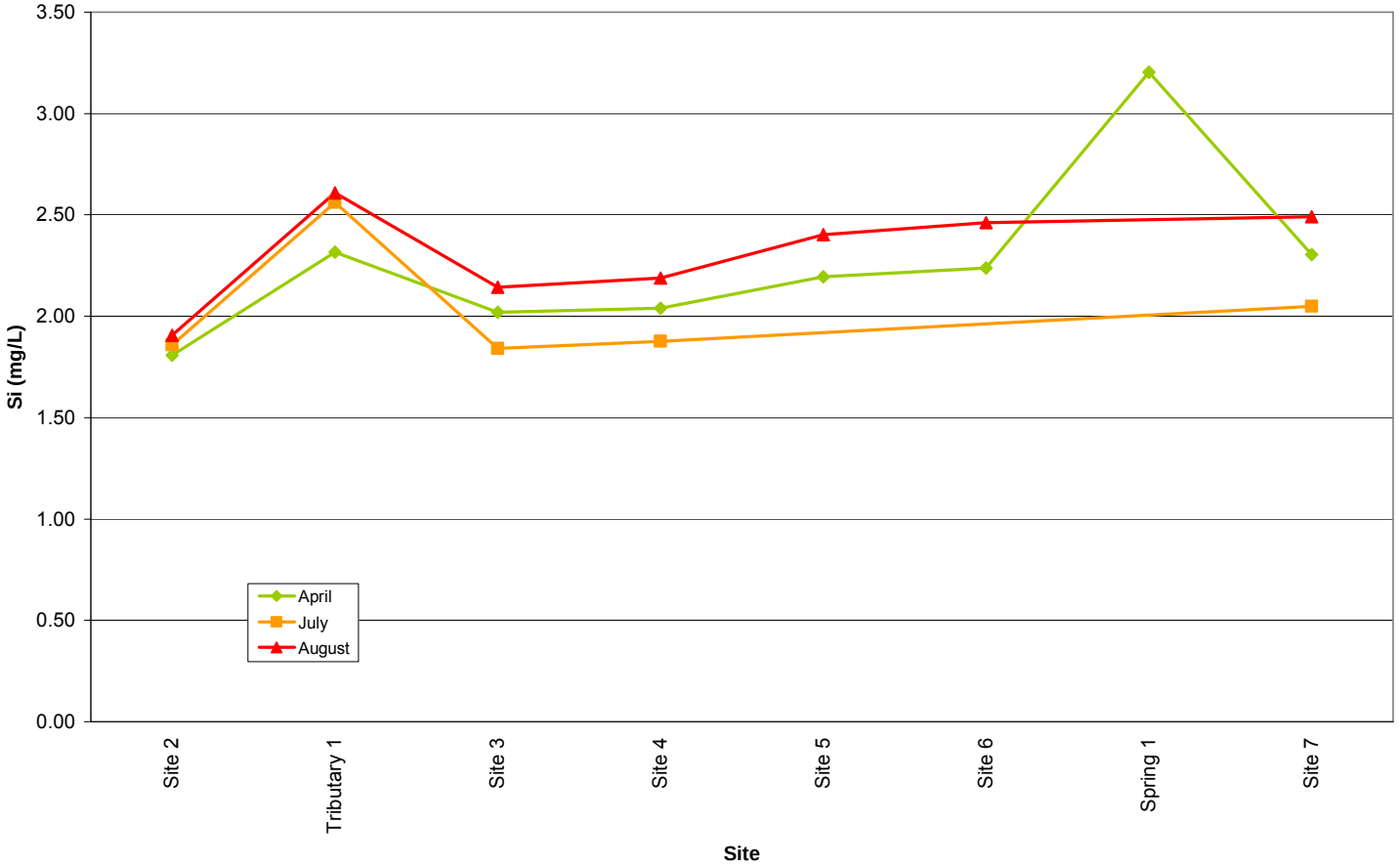

Figure 14. Si plotted against collection date

concentrations of these ions with distance from the headwaters suggested no significant inputs of this type below Tributary 1. Low relative levels of NO_3 (Figure 5) in the tributary may have been caused by a larger degree of uptake by vegetation and possible denitrification by subsurface microbiological activity (Silsbee and Larson 1982; Martin et al., 2001). Heightened levels of Si (Figure 13) were indicative of the water-rock interactions with a known geology of quartz and signified groundwater contribution to the tributary.

Site 2 was the highest site in the watershed and as expected displayed the most prominent effects of acid deposition of any of the in stream samples (Sullivan et al., 2007). Concentrations for pH and ANC were lower than any other in stream site (Figures 3 and 4) while SO_4 and NO_3 were higher (Figures 5 and 6). Higher relative concentrations of ions associated with acid-rock drainage or acid deposition induced leaching indicate these interactions probably occurred further upstream from the cascade. Site 2 water quality was determined to be closer to that of Tributary 1 than the other in stream sites due to these ion contributions.

Spring 1, designated as the second water type, was located between Site 6 and Site 7, the lowest site of the study. Sampling of this spring was possible for only the April collection date likely due to extreme drought conditions. Measured ionic concentrations in the spring were considered to be very low indicating shallow groundwater circulation (Soulby et al., 1999). pH and ANC values for Spring 1(Figures 3 and 4) were the highest for any site which would suggest interaction with subsurface materials, where water reactions with solid species might be consuming H^+ and also the relative lack of exposure to acid deposition. The highest levels of Na and Si of the study were measured for this site (Figures 7 and 13) furthering the assumption of a more extended groundwater interaction with the assumed subsurface of plagioclase feldspar and quartz.

Stream chemistry for, Sites 3 through 7, displayed a more muted signal than was distinguished for the point recharge waters. This indicates recharge to

the stream from alternate sources that may be diluting groundwater signals (Shand and Haria 2005). The lack of identified point recharge, such as large fracture networks intersecting the stream, and the diluted nature of in stream chemistries compared to that of the obtained focused sources are both indications of a large diffuse recharge component of stream flow.

Assumed diffuse recharge input from shallow soil water or shallow groundwater throughout the length of the stream would be expected to have a signature close to that of area precipitation. Throughfall precipitation chemistries, Table 1, were used for general comparison and as a check of chemical and hydrologic assumptions. Data from collection points close to Sites 6 and 7 and Sites 2, 3, and Tributary 1 were used in the analysis. Comparisons with Sites 2 and 3, and Tributary 1 displayed the influence of possible acid-rock drainage or deposition induced leaching on Tributary 1 in the lower pH and higher SO_4, Fe, and Mn concentrations relative to the throughfall. NO_3 levels were lower in the throughfall samples than the stream. This could be attributed to spatial variability in NO_3 deposition and the ability of collection techniques to accurately measure NO_3 throughfall. Si and Na concentrations in the stream were much higher than the throughfall sample indicating groundwater inputs at both compared sampling locations. Dolomite indicative ions, Ca and Mg, were lower in the stream than in throughfall which would be expected since no significant inputs of these ions were suspected in this area of the basin. The comparison with throughfall for Sites 6 and 7 showed overall concentrations, for parameters other than pH, ANC, Na, and Si, of throughfall precipitation were higher than stream values probably caused by the dilution of precipitation inputs by soil and groundwaters, which would also explain higher concentrations of the above mentioned ions. NO_3 levels in the stream samples for Sites 6 and 7 were again much higher for April than the throughfall samples. These precipitation comparisons led to the overall inference that groundwater and geology contribute to the chemistry of the stream and that dilution of precipitation and acid deposition constituents is occurring throughout the stream.

The sampling of Tributaries 2 and 3, conducted for only the August collection date, gave a more in-depth view of point contributions to the stream, however, values were only used qualitatively and were not included in the statistical analyses. The chemistries for Tributaries 2 and 3 were substantially different than the chemistry of Tributary 1, due in a large extent to assumed acid-rock drainage and deposition induced leaching inputs into Tributary 1. Tributary 2 displayed higher relative levels of Si and Na (Figures 14 and 15.) and also Ca and Mg (Figures 16 and 17.) which might be indicative of a small pocket of dolomite located in the drainage area above the tributary. Tributary 3, located between Sites 5 and 6, displayed a slightly different signature from that of Tributary 2 with no apparent dolomite interaction. Both tributaries displayed pH and ANC increasing influences (Figures 18 and 19.) shown by significant fluxes in these two parameters in the small length of stream between Sites 3 and 4 and between 5 and 6. NO_3 was also significantly lower for both of the tributaries due again possibly to relative higher amounts of vegetation uptake and denitrification (Figure 20.). Mass accretion (mg or µeq per second) was calculated for the in stream sites by using the cross-sectional flow data for each site provided in (McKenna 2007) multiplied by the concentration of solutes. This showed that the rate of solute mass flowing down the stream generally increased between Site 3 and 4 due to Tributary 2. Mass accretion increases were also noticed between Sites 5 and 6 at tributary 3, however these values were much smaller than for Tributary 2. Mass accretion figures are included in the Appendices. Non-uniform mixing of tributary water with stream water might create an area of shelter for fish during storm events when episodic acidification usually occurs. To determine possible chemical characteristics of that water a mass balance of equal amounts of each tributary water chemistry with the corresponding above tributary site chemistry, was calculated to determine what concentrations would be created from an equal mixing of the stream and tributary waters (Table 4.). These showed that areas containing equal amounts of each water, near the tributary outlets to the stream, would display water quality parameters with a 0.30 increase in pH and a 0.68 mg/L increase in

ANC at Tributary 2 and 0.80 and 1.07 mg/L at Tributary 3. These locations might display better water quality for fish during periods of extreme episodic acidification.

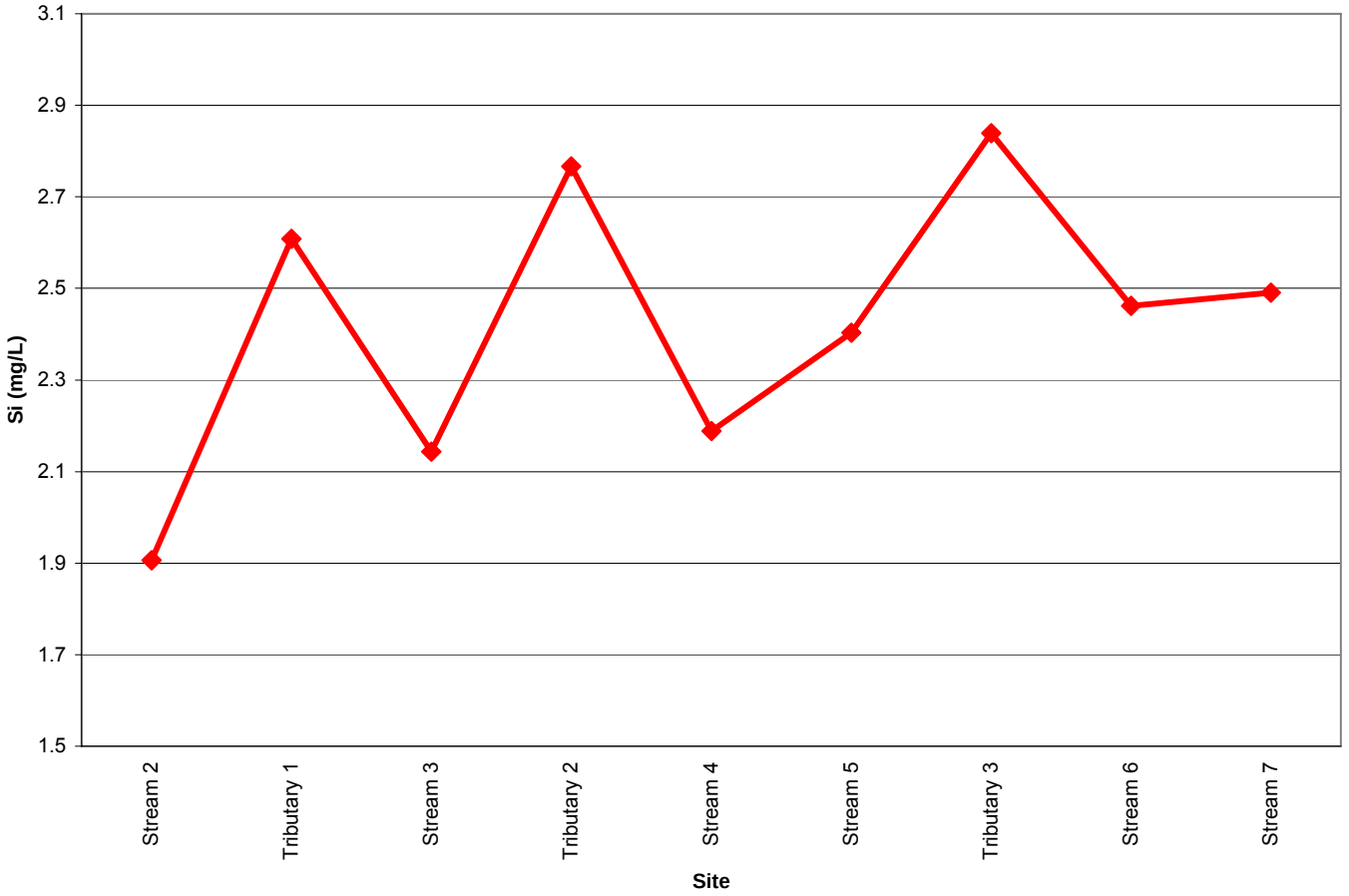

Figure 15. Si plotted against tributary and stream sites for August collection date.

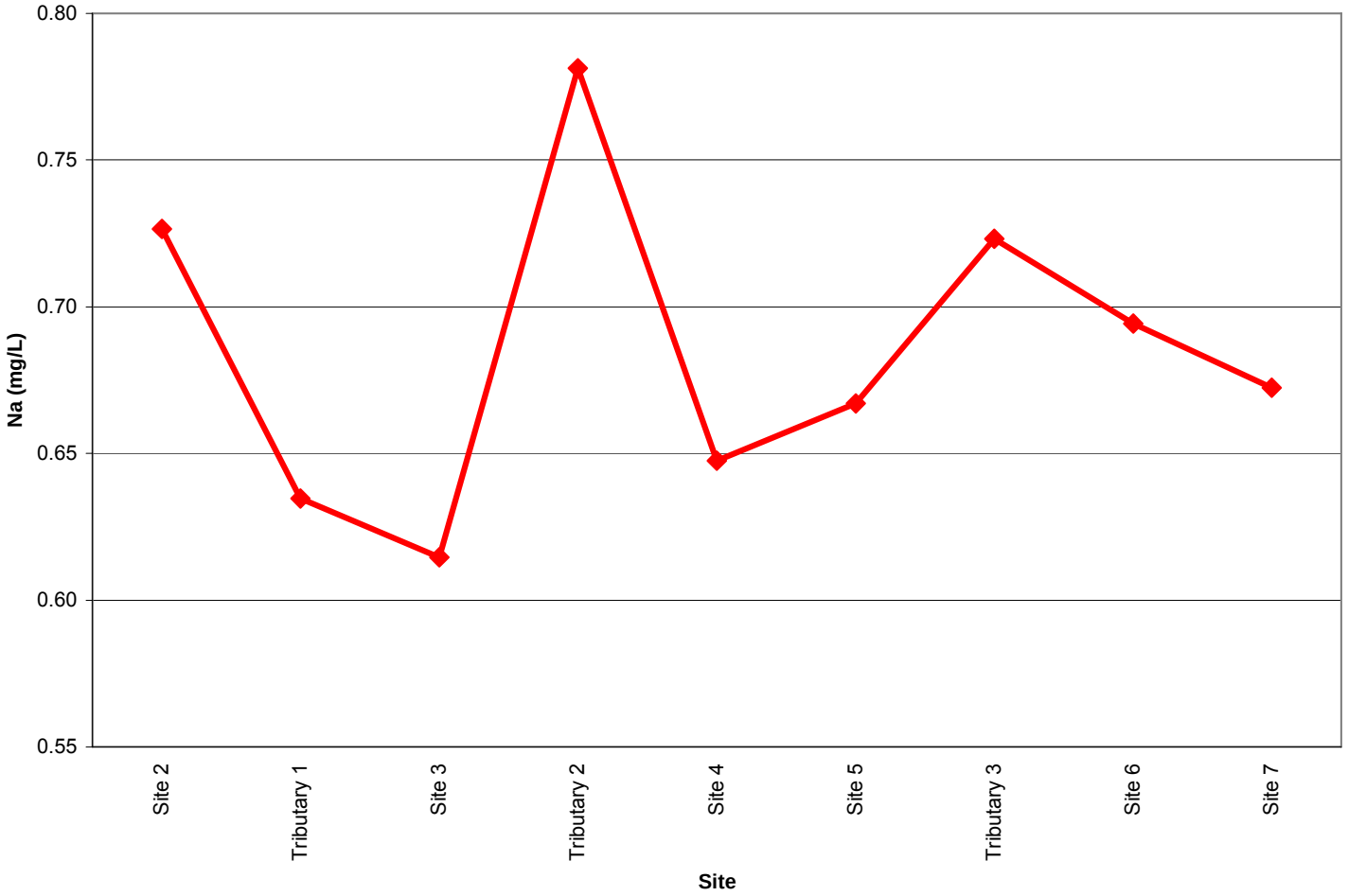

Figure 16. Na plotted against tributary and stream sites for August collection date.

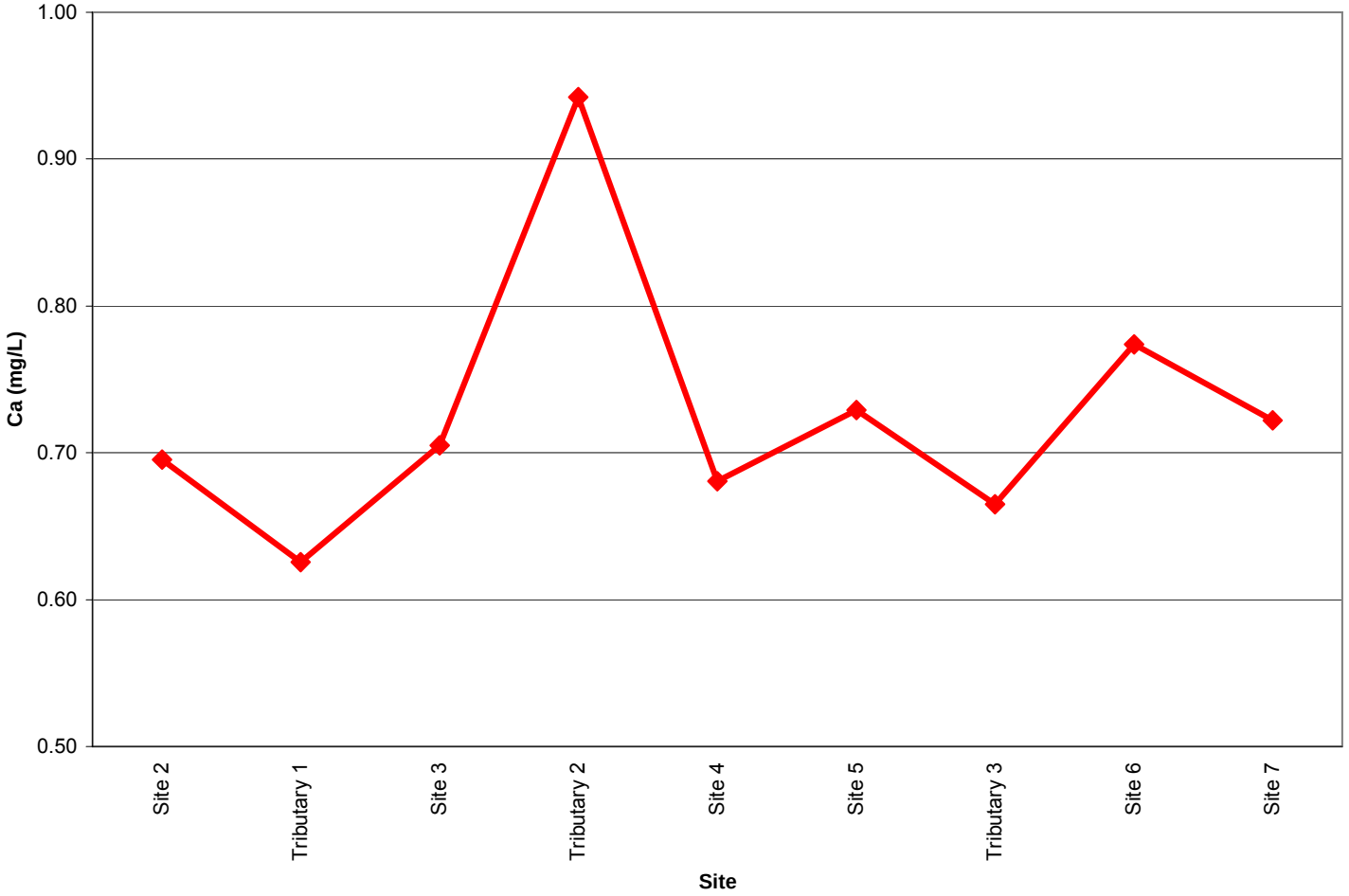

Figure 17. Ca plotted against tributary and stream sites for August collection date.

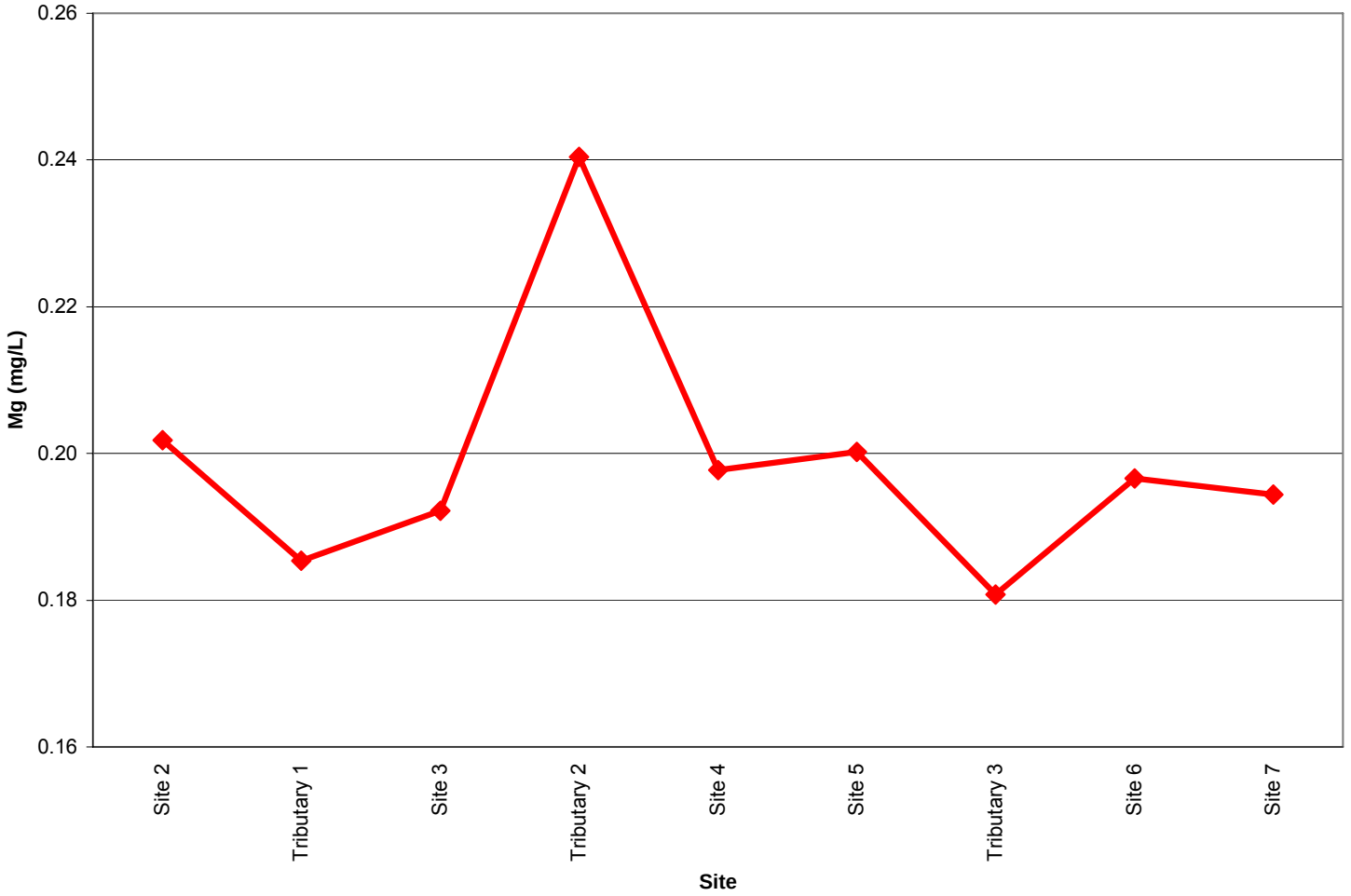

Figure 18. Mg plotted against tributary and stream sites for August collection date.

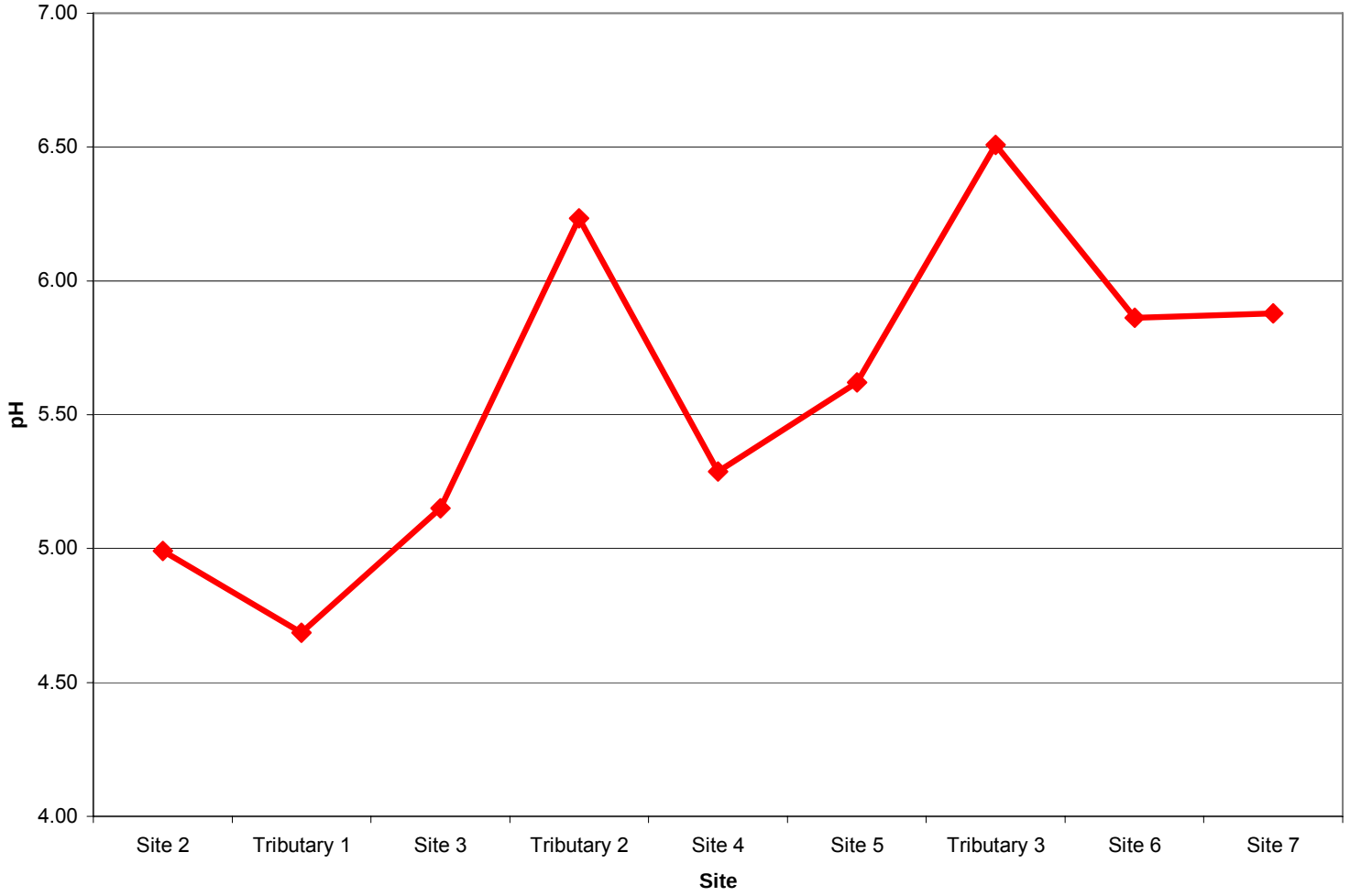

Figure 19. pH plotted against tributary and stream sites for August collection date.

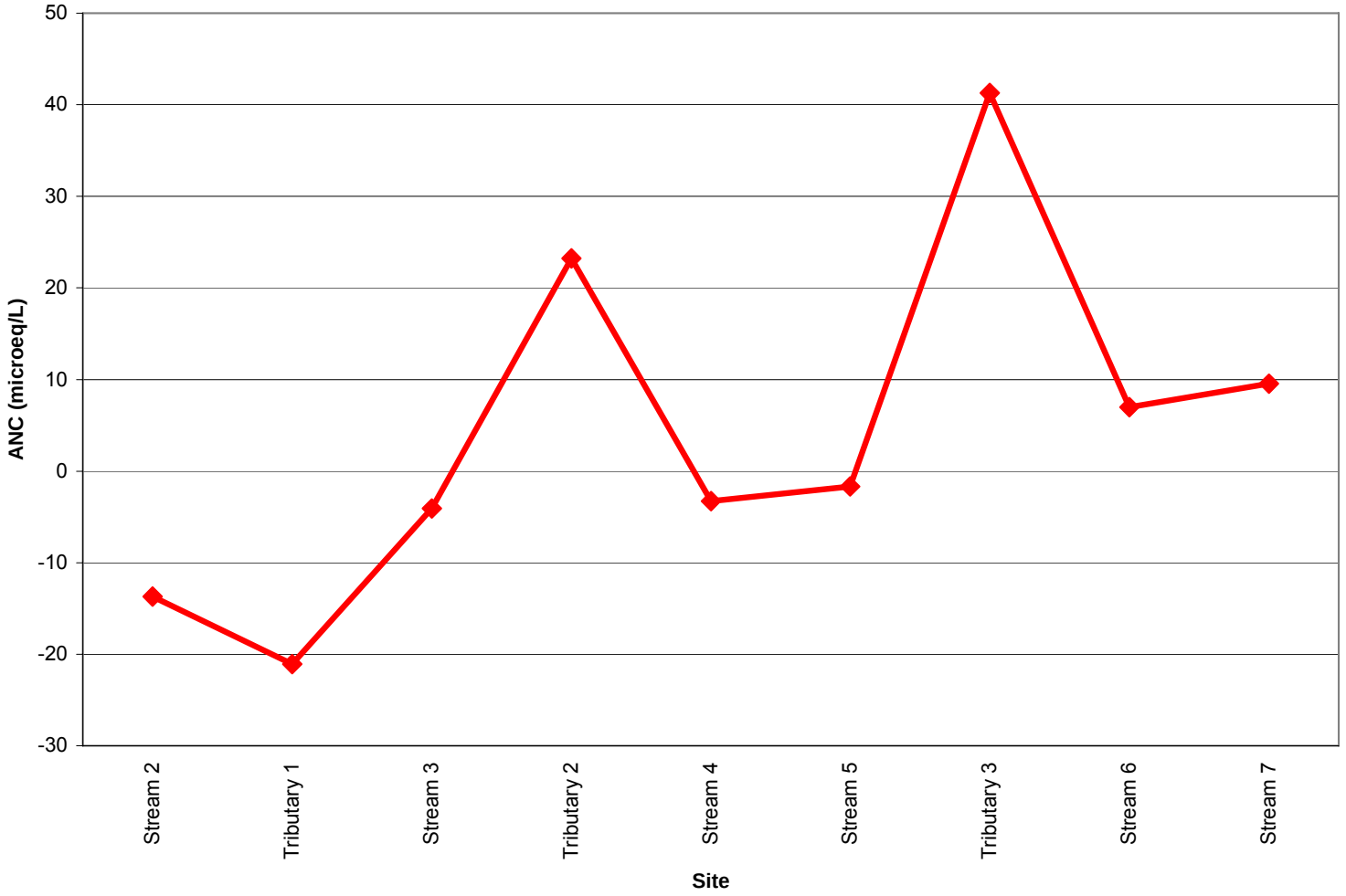

Figure 20. ANC plotted against tributary and stream sites for August collection date.

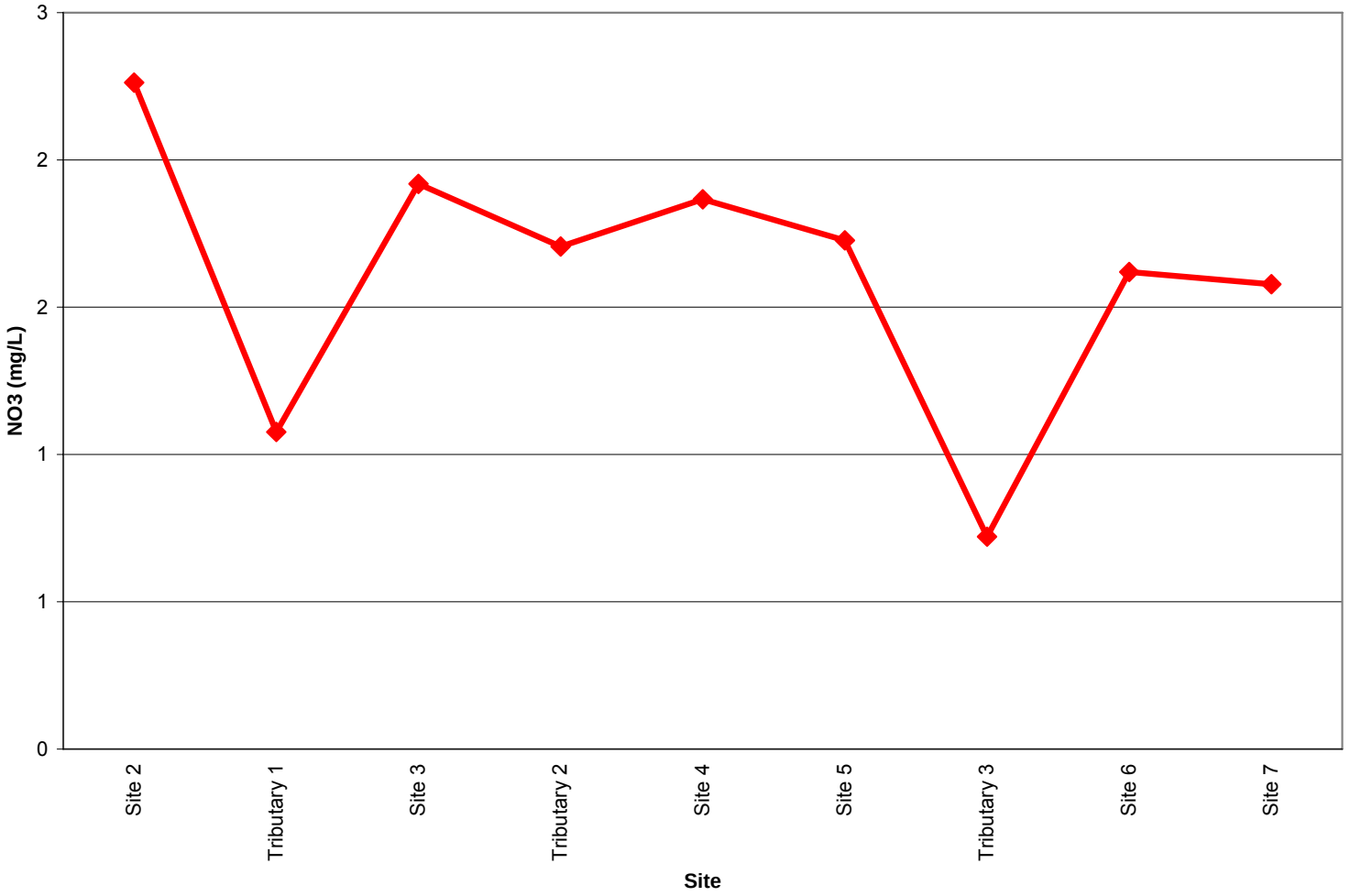

Figure 21. NO_3 plotted against tributary and stream sites for August collection date.

Table 4. Mass balance of stream and tributary chemistries.

ID	Month	pH	ANC	Conductivity	Nitrate	Sulfate	Sodium	Magnesium	Calcium	Aluminum	Silicon
			µeq/L	µs/cm				mg/L			
Stream 3	August	5.151	-4.108	13.800	1.9184	2.0801	0.615	0.192	0.705	0.106	2.144
Tributary 2	August	6.234	23.223	13.310	1.7063	1.5726	0.781	0.240	0.942	0.065	2.767
Balance	August	**5.700**	**9.558**	**13.555**	**1.812**	**1.826**	**0.698**	**0.216**	**0.824**	**0.085**	**2.455**
ID	**Month**	**pH**	**ANC**	**Conductivity**	**Nitrate**	**Sulfate**	**Sodium**	**Magnesium**	**Calcium**	**Aluminum**	**Silicon**
			µeq/L	µs/cm				mg/L			
Site 5	August	5.621	-1.697	12.540	1.7268	1.9389	0.667	0.200	0.729	0.093	2.404
Tributary 3	August	6.507	41.269	10.510	0.7212	1.0805	0.723	0.181	0.665	0.030	2.839
Balance	**August**	**6.200**	**19.786**	**11.525**	**1.224**	**1.510**	**0.695**	**0.190**	**0.697**	**0.062**	**2.621**

Temporal Variations in Parameters:

The study was designed to catch temporal variations in stream chemistry by the collection of samples in typically extreme months of the year. This was not the reality, however, due to the extreme drought conditions in place over the duration of the study period. The data collected has, therefore, been analyzed with the level of drought at collection time taken into account. While the overall seasonal trends of precipitation were not altered (i.e. August was the driest month), it would be expected that concentrations would normally be greatly muted with the much higher flow conditions and that ephemeral springs such as Spring 1 in the study might contribute much more point recharge and therefore chemistry to the streams under these conditions. Table 5 shows precipitation levels at collection dates for the general area and also the average values of precipitation for the months in question. August was the driest month followed by July and then April.

Temporal variations in sample chemistry generally followed the same spatial patterns in the study area while displaying a diverse pattern of changes in overall concentrations relatively over the three collection dates. Water-rock interaction parameters Si and Na (Figures 7 and 13.) were highest on the August collection date. This is attributed to groundwater making up a larger percentage of stream water (Silsbee and Larson 1982). Levels of Ca and Mg ions in the stream (Figures 8 and 9.), associated with dolomite deposits in the area, followed a trend of decreasing concentration from April through August. This is possibly due to lack of proper conditions for redox reactions on the drier, warmer collection dates. Ions assumed to be associated with acid-rock drainage or acid deposition inrduced leaching, SO_4, Al, Fe, and Mn all displayed highest concentrations in July (Figures 6 and 10-12.) which might be explained by a combination of relatively more precipitation than August and therefore higher concentrations in tributary waters flowing into a less precipitation-diluted stream than April. Acid deposition parameters, pH and ANC, displayed higher concentrations on the August collection date (Figures 3 and 4.) signifying

Table 5. Precipitation data for Gatlinburg, Tennessee 1971-2000 and 2007.

Precipitation Data				
Date	**Year to Date (mm)**	**Previous 30 Days (mm)**	**Previous 7 Days (mm)**	**Calendar Month (mm)**
April				
4/10/2007	136.40	86.61	23.88	56.64
Average	373.13	-	-	110.74
July				
7/10/2007	233.40	83.57	2.29	56.64
Average	625.60	-	-	154.18
August				
8/7/2007	387.80	59.44	4.32	10.90
Average	927.61	-	-	116.59

groundwater dilution and buffering and also the lack of deposition in the form of precipitation. NO_3, also assumed to be an acid deposition input, was lowest in August (Figure 5) probably due to lack of precipitation deposition but also possible increases in plant NO_3 uptake and denitrification in the subsurface.

Five variables used in the initial investigation were either found to be incorrectly assumed to be major ions in the system or were determined to be too variable for the nature of this comparison. These ions were not used in the relative analysis. Plots for these ions are located in the Appendices. K was assumed to derive from water interaction with the K-feldspar of the area, and upon examination concentrations showed a large degree of spatial variability that might be attributed to varying amounts of the ion in equilibrium due to residence times and flow paths within the system. This scenario would explain the unpredictable pattern of K concentrations. The degree of variability in the concentrations prevented analysis for the comparative nature of this study. Cl was the exception to correlations in acid deposition constituent trends and is assumed to vary randomly with season and spatial trends of deposition and experience little alteration with stream interaction as opposed to some of the other ions. These factors made drawing a meaningful conclusion from relative site and temperal comparisons difficult. Zn was another ion that did not display significant trends or correlations that would lead to the determination of processes causing its signature in the stream. The trace amounts found in sampling are assumed to most likely be environmental inputs that vary greatly by area and season. Finally, NH_4 has been shown to be greatly retained in the canopy and soil of the park (Miegroet et al., 2001). Only five NH_4 samples out of the three sample dates were at concentrations high enough for detection. This led to removal from the analysis due to the inability to comparatively analyze concentrations. Cu was present at levels too low for detection and was not use in analyses.

Statistical Analysis:

Figures 21 though 23 show scatter plots with corresponding correlation coefficients for bivariate combinations of ion concentrations. Correlations were investigated using both the global data set and the data set from each collection date. The ellipse around samples in each scatter plot indicates the area encompassing 95% of the samples. The shape of the ellipse depicts high correlation of the variables by collapse along the diagonal axis. Rounded and non-diagonal ellipses signify uncorrelated variables. Examination of sample correlations for the three collection dates collectively supported many of the previously made temporal and spatial chemistry inferences. Si and Na were moderately correlated (r_{xy} = 0.77) (Figure 21.) which could be explained by some heterogeneity in geology between the quartz and feldspar. Ca and Mg correlated well (r_{xy} =0.91) and also displayed high correlation with NO_3 ($r_{xy} = 0.92$ and $r_{xy} = 0.90$) respectively (Figure 21). This may be due similar conditions acting on both parameters such as the lack of biological activity and NO_3 uptake taking place in areas where dolomite weathering is prominent leading to higher concentrations than other areas of the system. This trend was also displayed in Tributaries 2 and 3 for August. SO_4, Al, Fe, and Mn all correlated well ($0.67 \le r_{xy} \le 0.97$) (Figure 22.) which would be expected from acid drainage water or acid induced leaching, with the exception of Mn and Fe ($r_{xy} = 0.39$) possibly due spatial variability in the inputs of Fe. Tributary 1 samples displayed the best correlation for these ions due most likely to the acid-rock drainage parameters and higher amounts of ions in the tributary.

Finally, possible acid deposition parameters, pH, ANC, NO_3, and SO_4 (Figure 23), showed relatively high positive correlation between pH and ANC (r_{xy} =0.71) and moderate negative correlation between SO_4 and pH (r_{xy} =-0.57) and a high negative

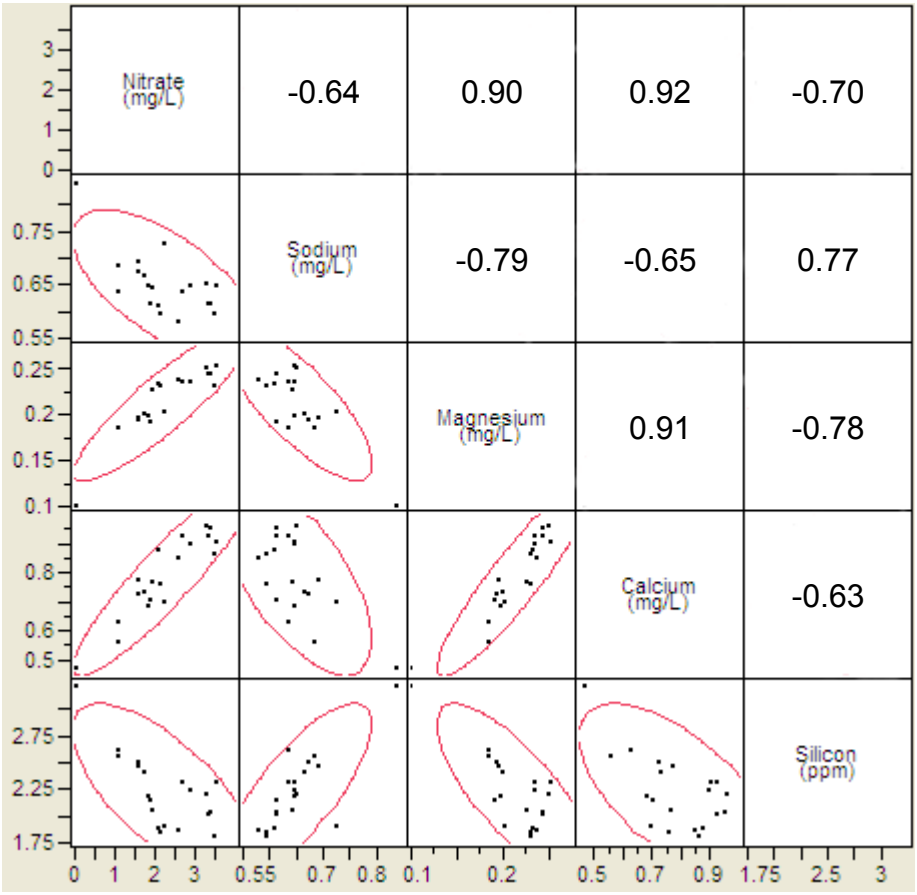

Figure 22. Global dataset for Dolomite and Water-Rock ions.

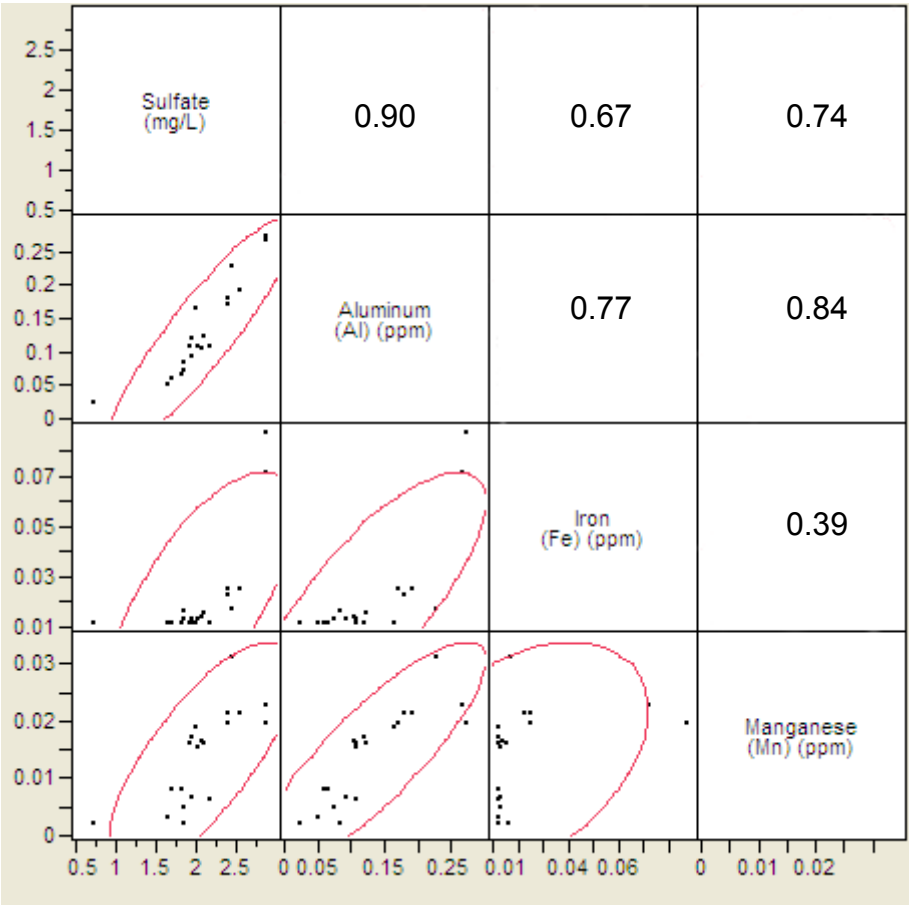

Figure 23. Global dataset for Acid Rock Drainage ions.

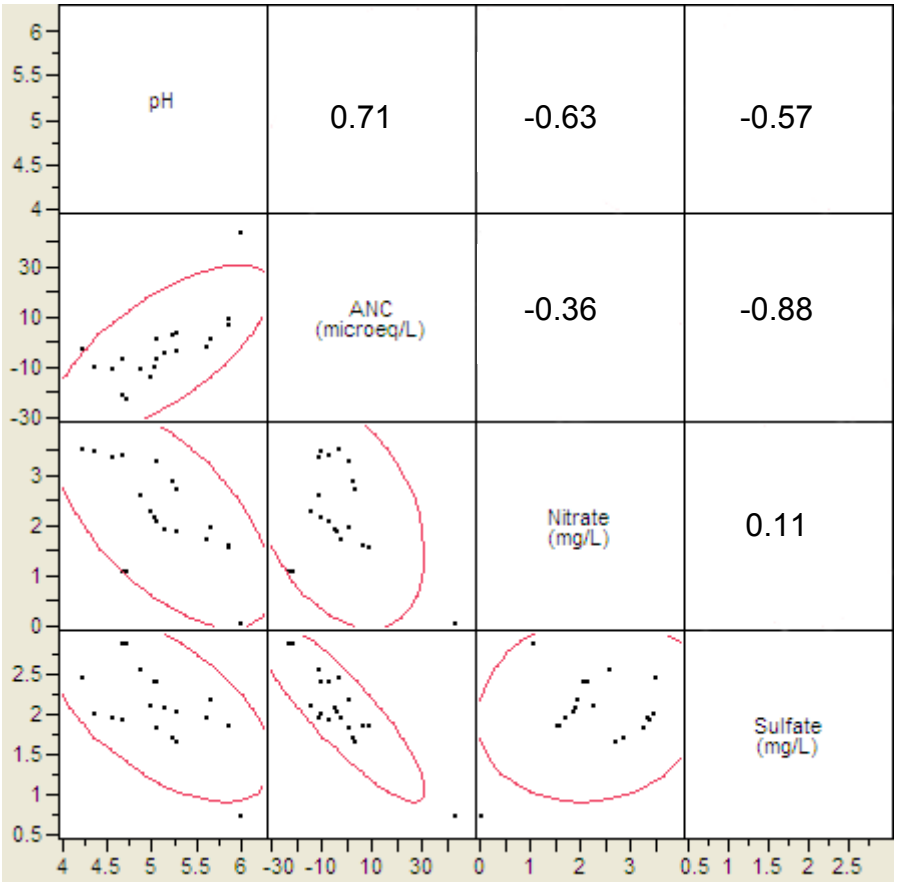

Figure 24. Global dataset for Acid Deposition ions.

correlation between SO_4 and ANC (r_{xy} =-0.88). NO_3 correlated poorly with the three other parameters at -0.63, 0.11, and -0.36 for pH, SO_4, and ANC, respectively. This may be explained by variability in denitrification and NO_3 uptake by vegetation and in spatial differences in NO_3 deposition.

Temporal trends were also delineated by comparing correlation matrices for the individual sampling dates and are provided in the Appendices. Correlations as a whole did not alter significantly between collection dates and almost entirely supported previously made inferences.

Conceptual Model:

Water chemistry in Ramsey Prong showed the influences of multiple sources and interactions without one major identifiable contributor. Acid deposition, acid-rock drainage or acid deposition leaching, and groundwater-surface water interactions all appeared to play a role in stream water quality. Samples at the top of the watershed, Site 2 and Tributary 1, displayed chemistries that were likely linked to acid deposition and acid-rock drainage or acid deposition leaching. Moving down by site through the watershed, acid associated chemistries were diluted by groundwater and shallower, diffuse recharge. These inputs resulted in higher ANC and pH (shown spatially in Figure s 23 and 24.) and also the addition of ions associated with groundwater and water-rock interactions. Tributaries 2 and 3 were found to have stream buffering capabilities and slightly different ion contributions relative to the global data set. Spring 1, located near the bottom of the study area, displayed the most chemically unique signature and is suspected as being the sample most indicative of point groundwater contributions to the stream.

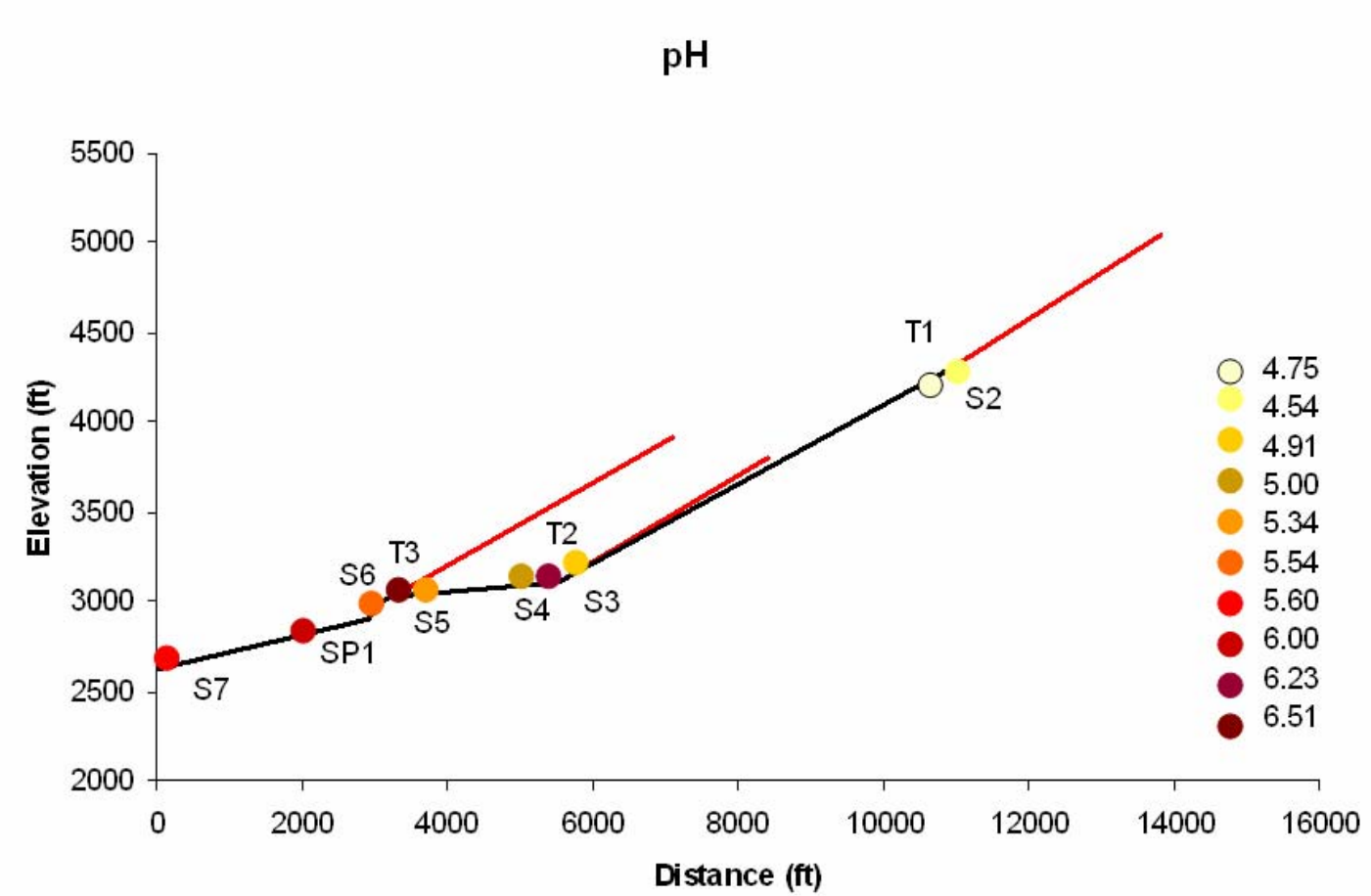

Figure 25. pH values plotted on a spatial representation of the study area in elevation and distance from Site 7. Ramsey Prong is represented by a black line while Tributaries 1-3 are represented with a red line.

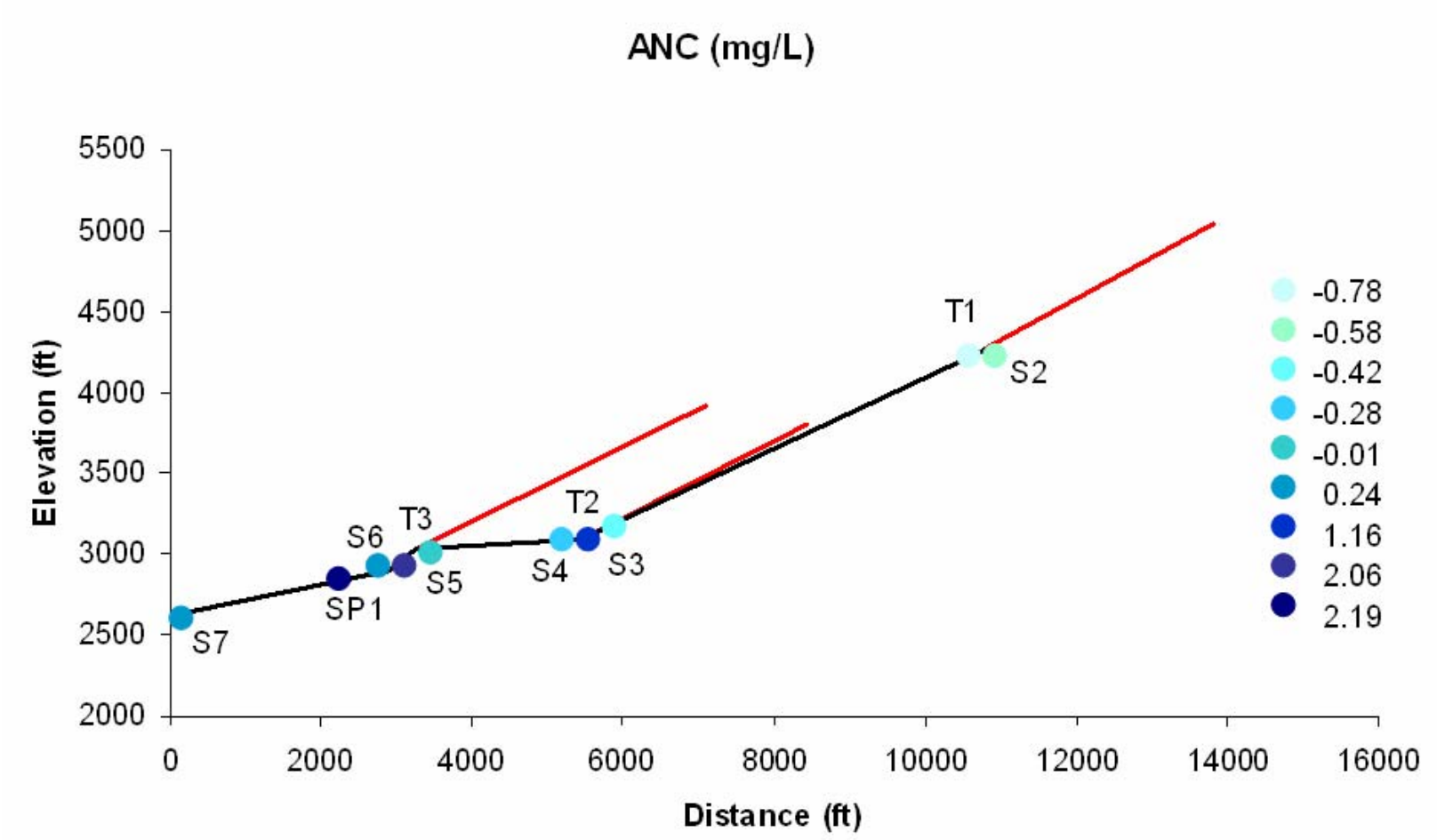

Figure 26. pH values plotted on a spatial representation of the study area in elevation and distance from Site 7. Ramsey Prong is represented by a black line while Tributaries 1-3 are represented with a red line.

CONCLUSION

This study demonstrated the use of limited sampling as a tool to characterize an upland catchment where conventional field techniques could not be utilized. A conceptual model of the area was successfully developed by a relative comparison of values from eight sampling sites and two tributaries. Multivariate statistics were also found to be a useful for recognizing correlations and, further, water types in the data. The sampling sites were delineated into three different water types and inferences about the types of water-rock interaction, residence times, flow paths, and general chemistry of the study basin were possible. It was concluded that groundwater, while playing a major role in stream water generation, was primarily recharged directly to the stream from shallow, diffuse sources that did not display individually identifiable buffering capacities, however, additions of tributary chemistries were shown to be buffers of stream quality and are believed to be primarily composed of point recharge spring waters and groundwater inputs. These tributaries appeared to be resilient to the severe drought conditions of the study period further emphasizing their groundwater sources but also their importance in this upland stream system. Overall, water quality at the lower elevations of the study area showed indications of being more suitable to support a healthy stream ecosystem.

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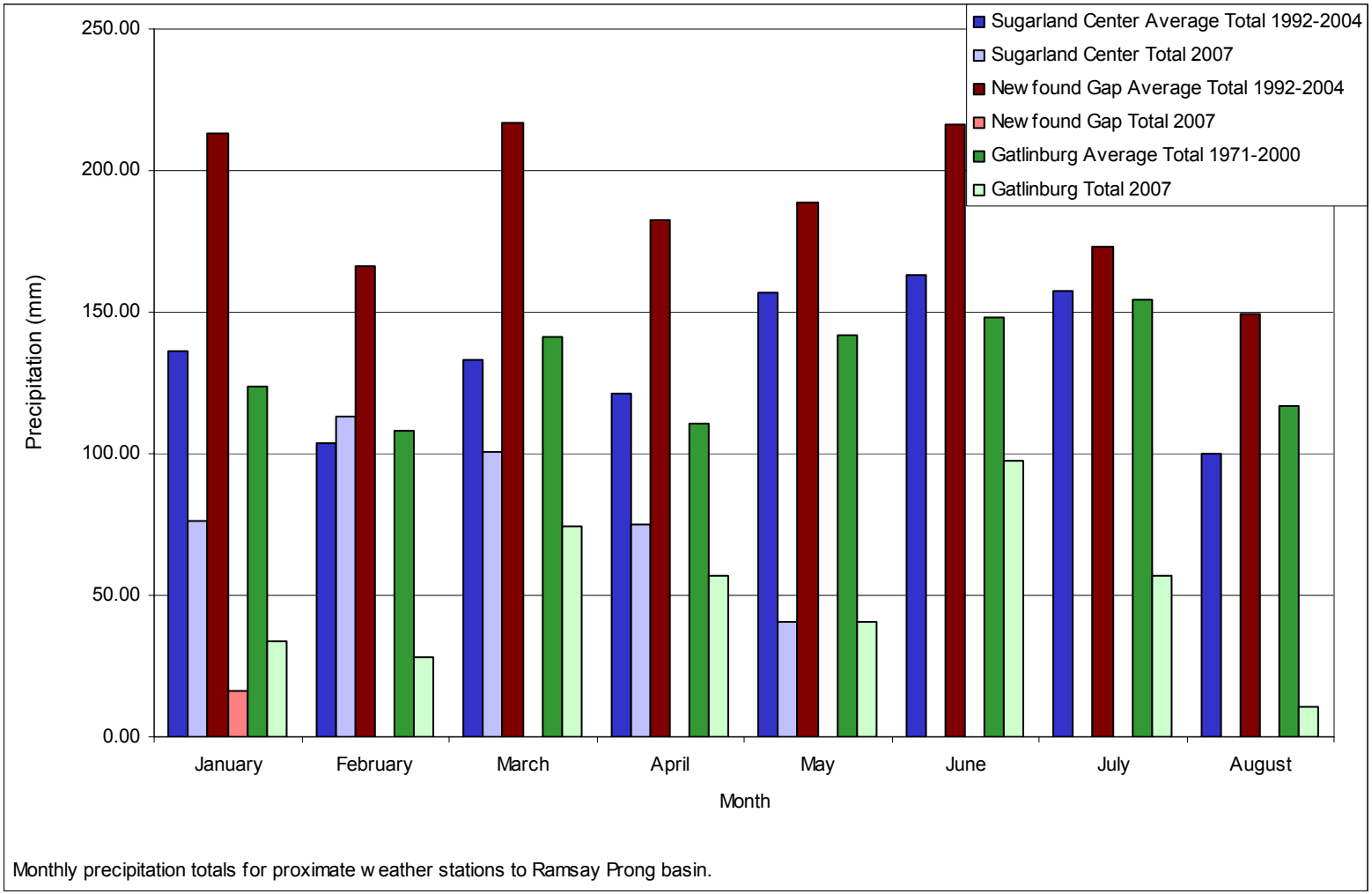
APPENDICES

Precipitation comparisons for locations within the park. (McKenna 2007)



Monthly precipitation totals for proximate w eather stations to Ramsay Prong basin.

Mass Accretion by Site for April.

Site	Flow	Flow	Nitrate	Sulfate	Sodium	Potassium	Magnesium	Calcium	Aluminum	Iron	Manganese	Silicon
	ft^3/s	(L/s)	mg/s									
Site 2	0.35	10.04	35.11	20.05	5.97	BDL	2.33	8.68	1.67	BDL	0.19	18.16
Site 3	3.59	101.63	339.74	196.93	62.15	970.99	24.75	93.73	12.25	BDL	1.71	205.25
Site 4	5.48	155.29	525.00	297.31	101.47	788.78	38.03	147.45	16.77	BDL	2.44	316.65
Site 5	2.53	71.60	234.53	130.40	46.42	737.72	17.88	68.85	4.76	BDL	0.60	157.11
Site 6	2.85	80.57	232.78	136.81	51.26	448.92	18.99	72.33	4.75	BDL	0.62	180.24
Site 7	8.31	235.35	638.12	390.45	152.60	1594.74	55.47	216.95	11.92	BDL	0.69	542.14

Chloride	Ammonium	Zinc
mg/s		
3.75	0.08	0.25
40.62	0.53	2.34
61.37	1.06	3.73
28.54	0.36	1.77
32.65	BDL	2.075
91.70	0.80	5.03

Mass Accretion by Site for July.

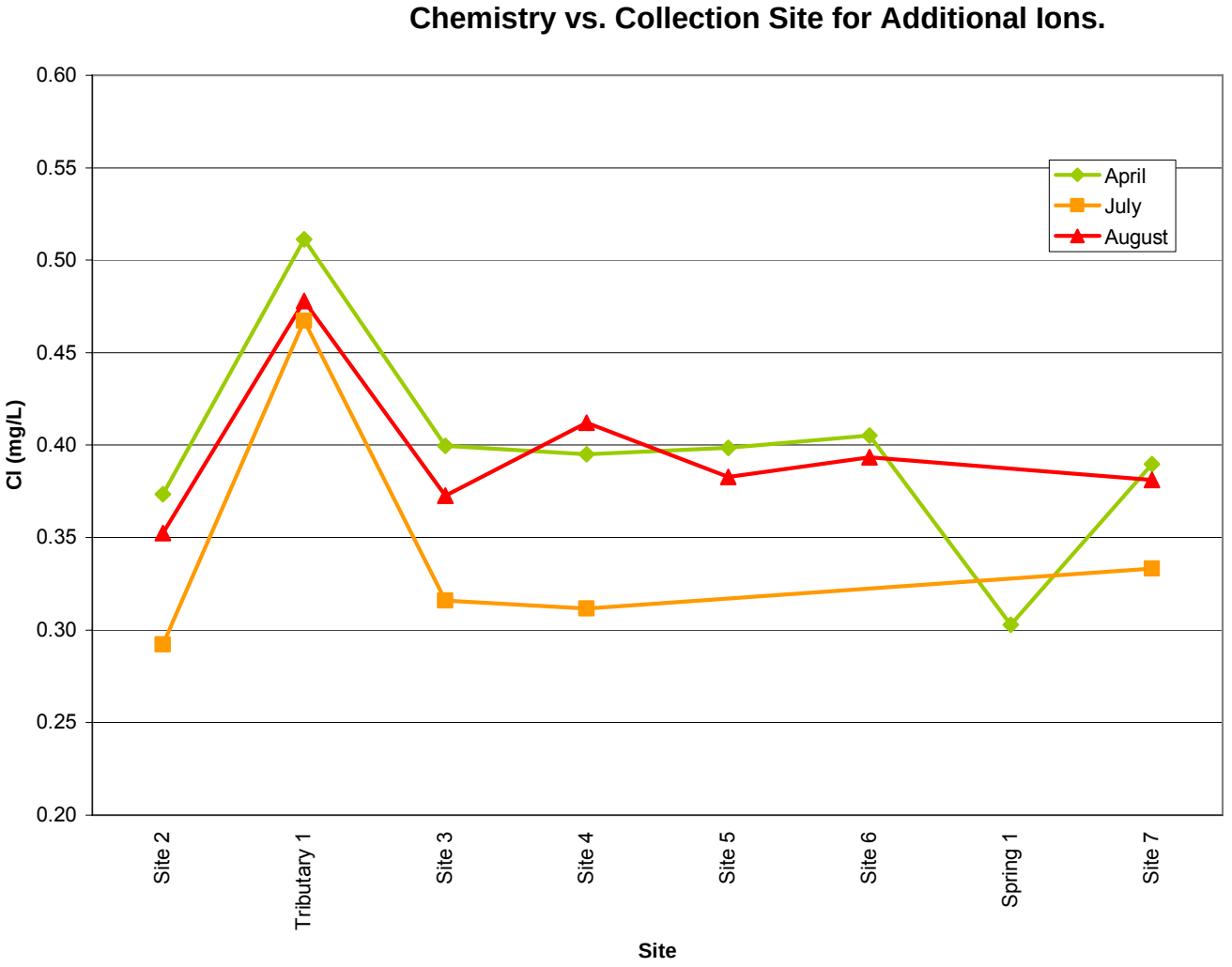
Site	Flow	Flow	Nitrate	Sulfate	Sodium	Potassium	Magnesium	Calcium	Aluminum	Iron	Manganese	Silicon
	ft^3/s	(L/s)	mg/s									
Site 2	3.46	97.98	254.98	250.48	56.73	24.98	23.21	83.39	18.787	2.477	2.083	182.09
Site 3	4.70	133.10	289.28	320.70	79.07	65.45	30.74	100.87	22.572	3.292	2.592	245.01
Site 4	7.49	212.21	440.80	511.62	129.58	72.08	49.50	185.39	38.218	4.856	4.540	398.14
Site 7	4.91	138.92	273.47	303.73	89.55	62.92	31.54	106.03	15.108	1.718	0.881	284.77

Chloride	Ammonium	Zinc
mg/s		
28.64	BDL	1.55
42.03	BDL	3.01
66.12	1.34	4.98
46.31	BDL	4.87

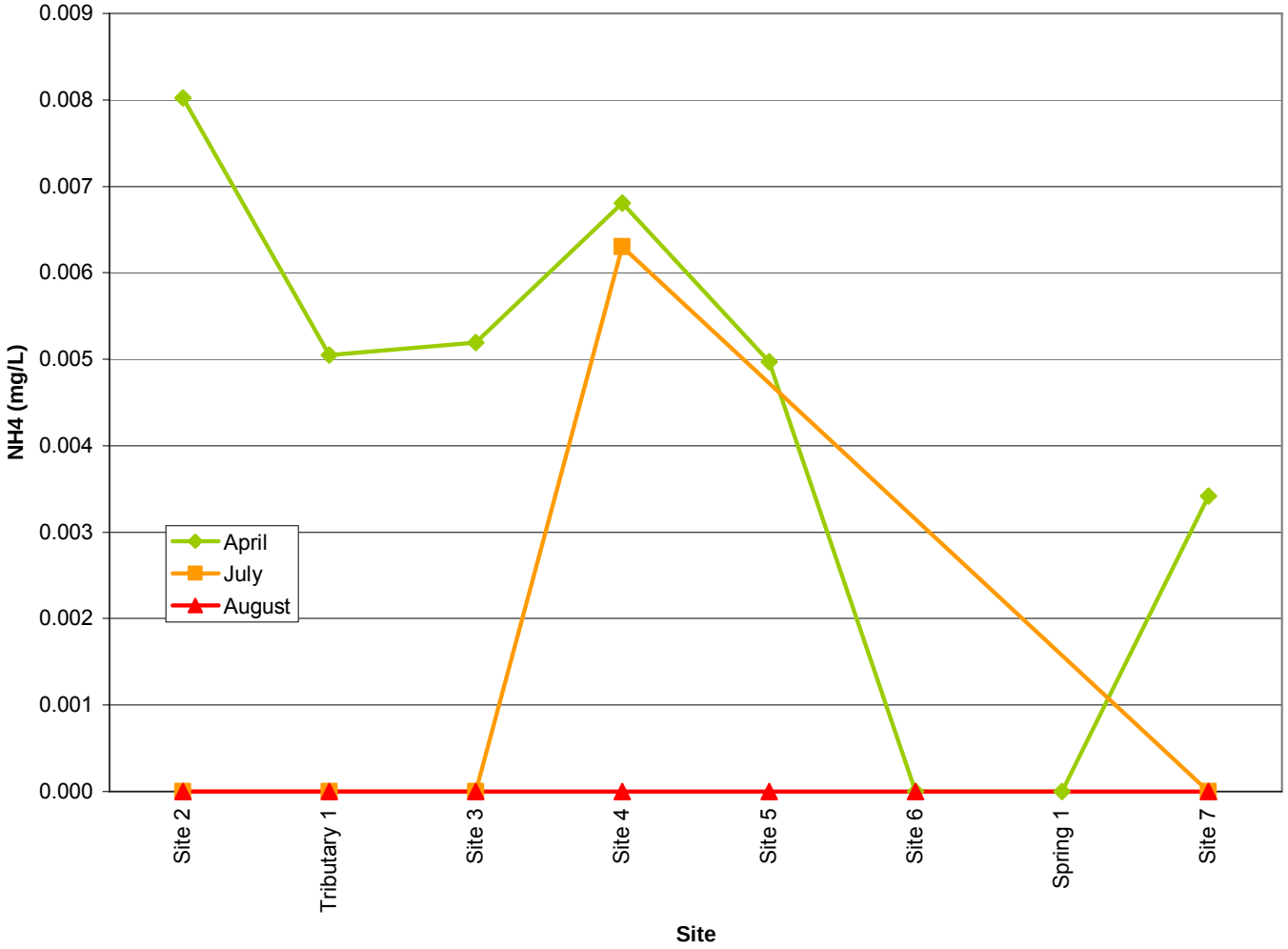
Mass Accretion by Site for August.

Site	Flow	Flow	Nitrate	Sulfate	Sodium	Potassium	Magnesium	Calcium	Aluminum	Iron	Manganese	Silicon
	ft^3/s	(L/s)	mg/s									
Site 2	1.50	42.61	96.42	89.94	30.96	12.83	8.60	29.64	5.26	0.66	0.69	81.21
Site 3	1.74	49.30	94.59	102.56	30.30	10.28	9.47	34.76	5.24	0.70	0.81	105.71
Site 4	2.17	61.47	114.70	124.75	39.80	BDL	12.15	41.83	6.56	0.81	0.96	134.53
Site 5	4.48	126.82	218.99	245.89	84.59	BDL	25.39	92.46	11.82	1.66	0.84	304.82
Site 6	6.51	184.33	298.54	342.17	127.97	35.98	36.24	142.66	13.56	2.42	0.92	453.86
Site 7	25.54	723.24	1141.51	1338.55	486.26	191.36	140.60	522.23	60.80	12.00	BDL	1801.67

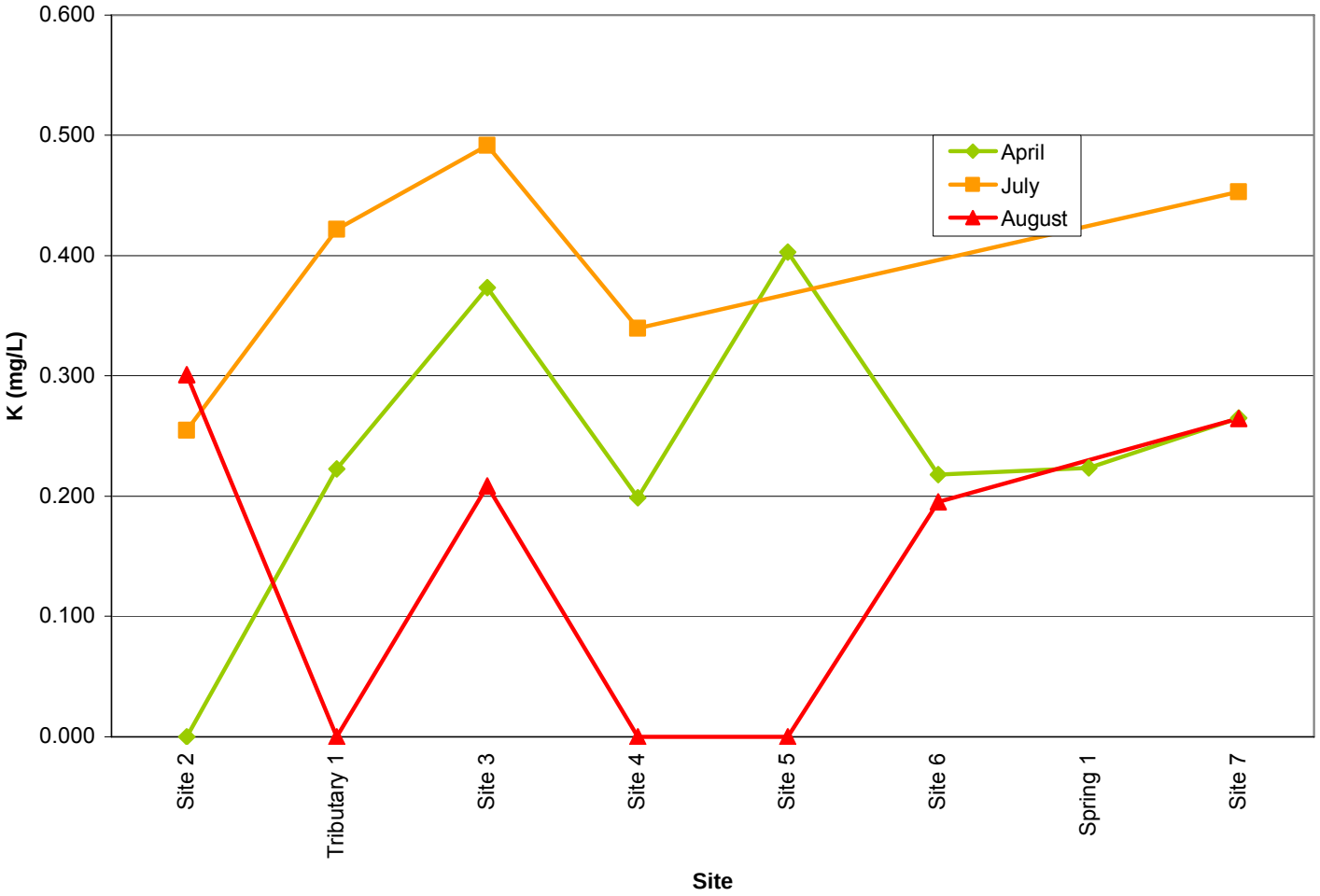
Chloride	Ammonium	Zinc
mg/s		
15.01	BDL	0.78
18.37	BDL	0.48
25.34	BDL	0.92
48.55	BDL	2.24
72.55	BDL	3.76
275.68	BDL	13.58



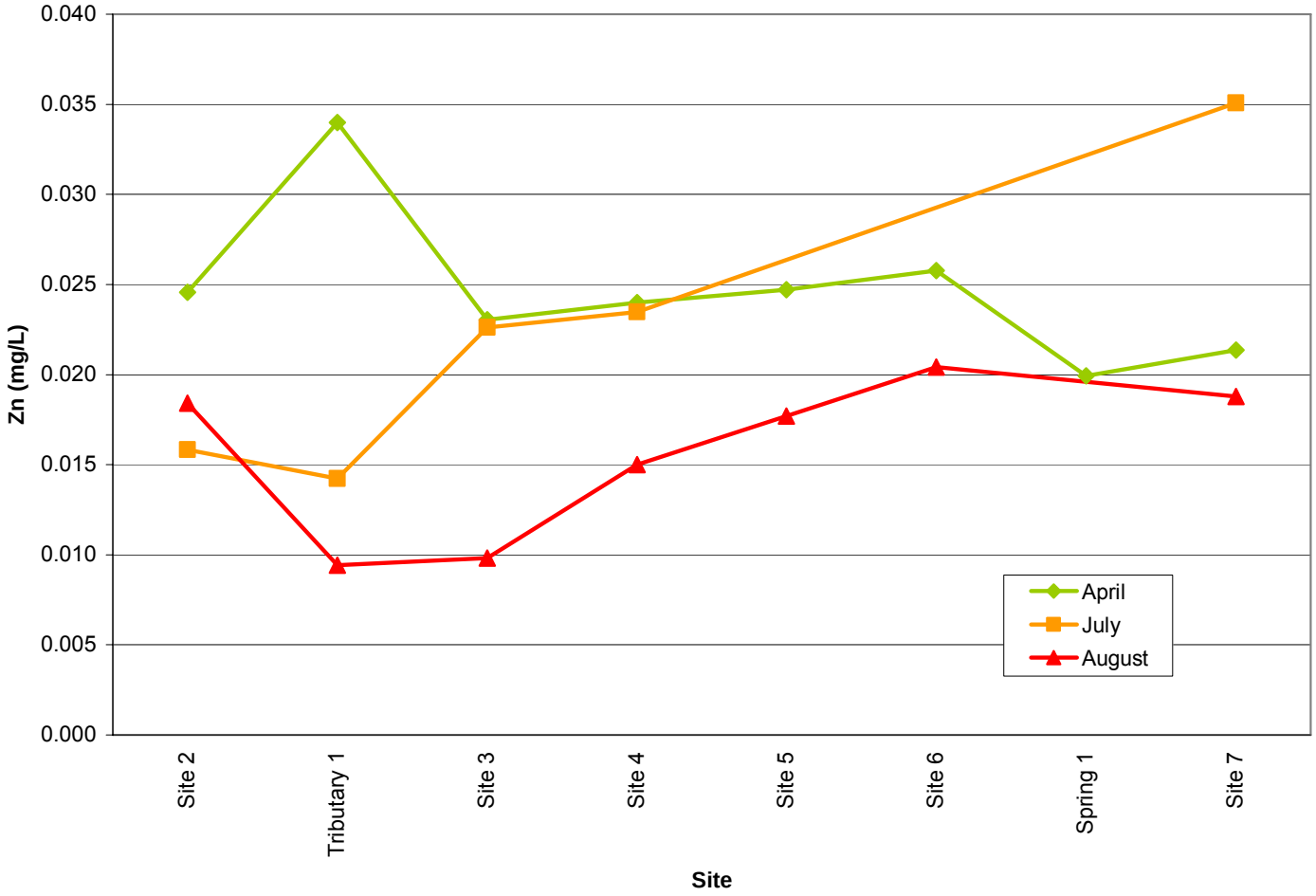
Cl plotted against collection date.



NH_4 plotted against collection date.

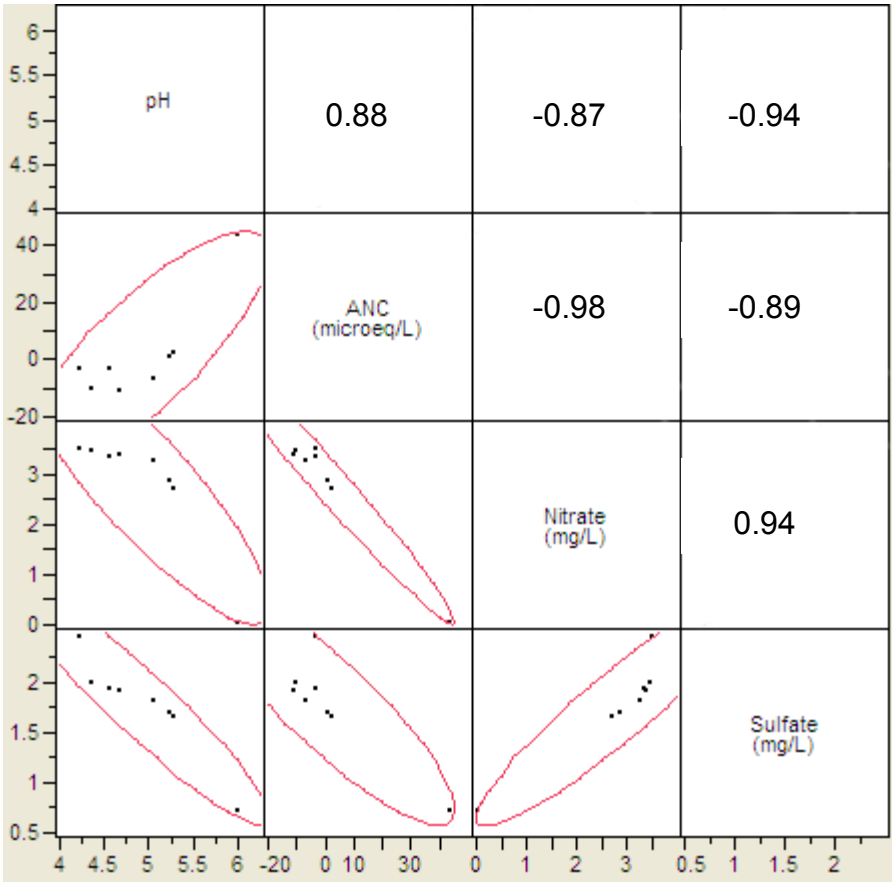


K plotted against collection date.

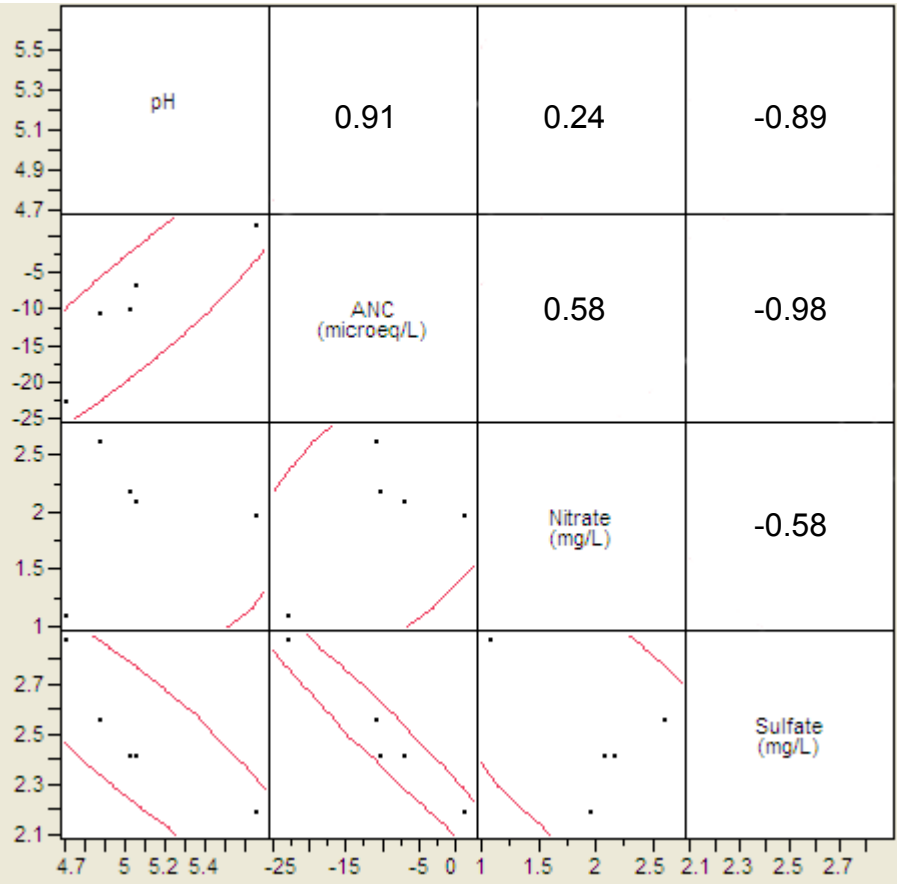


Zn plotted against collection date.

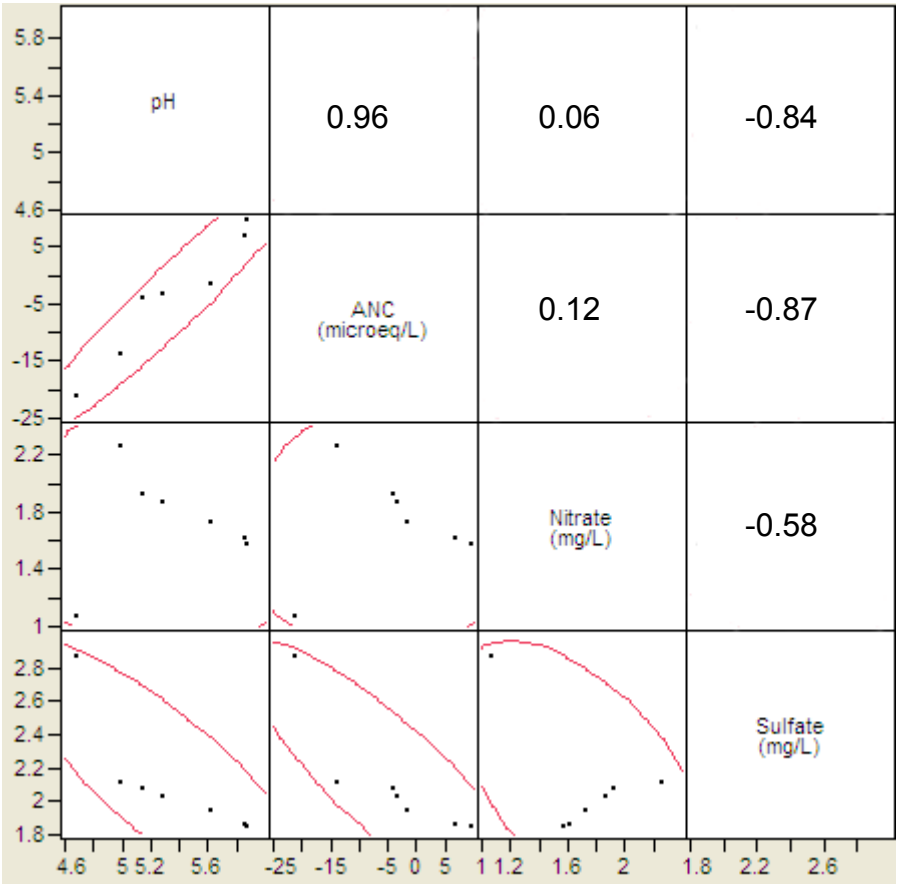
Temporal bivariate plots for ion combinations.



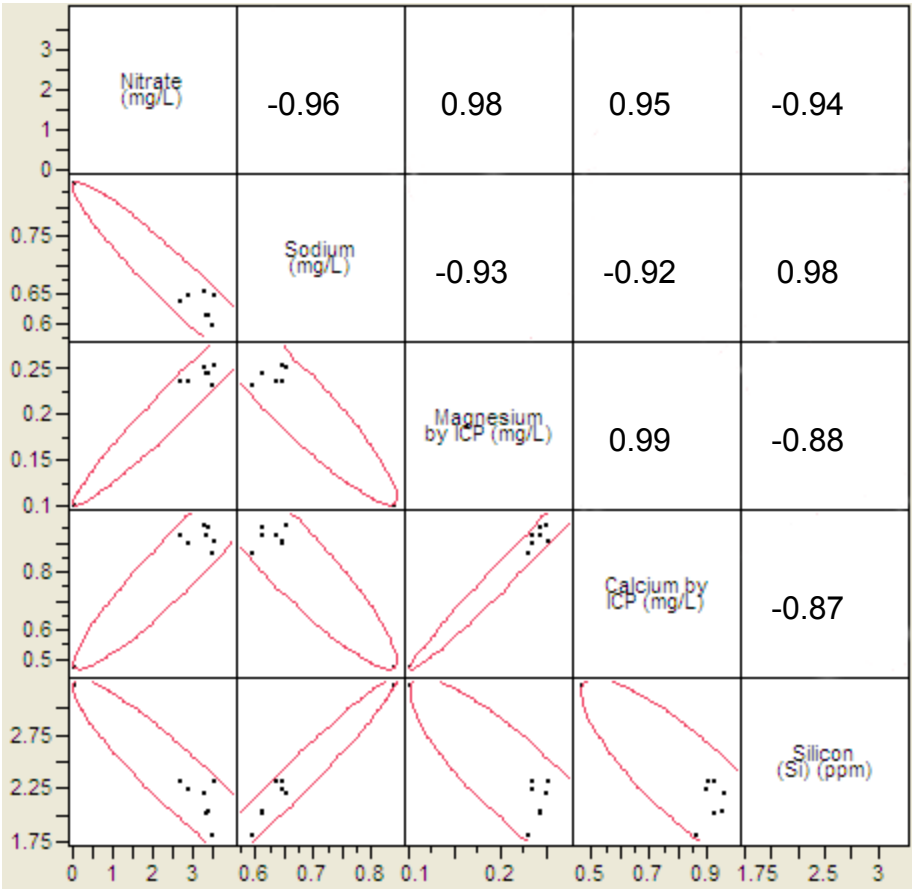
April dataset for Acid deposition ions.



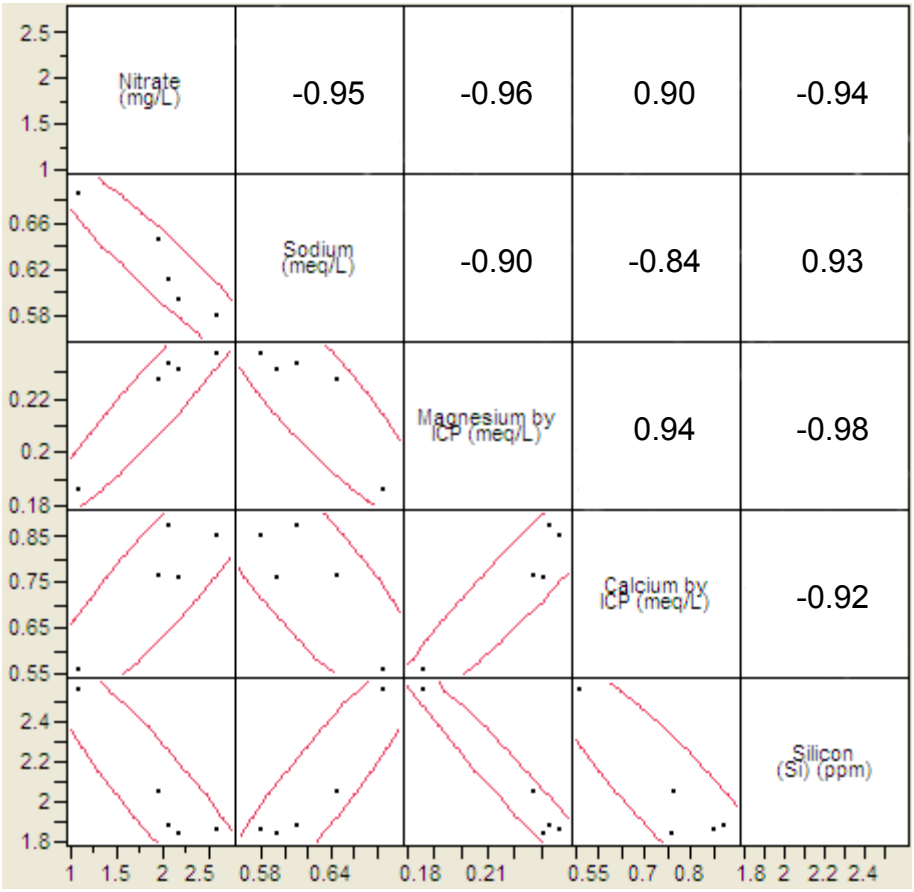
July dataset for Acid deposition ions.



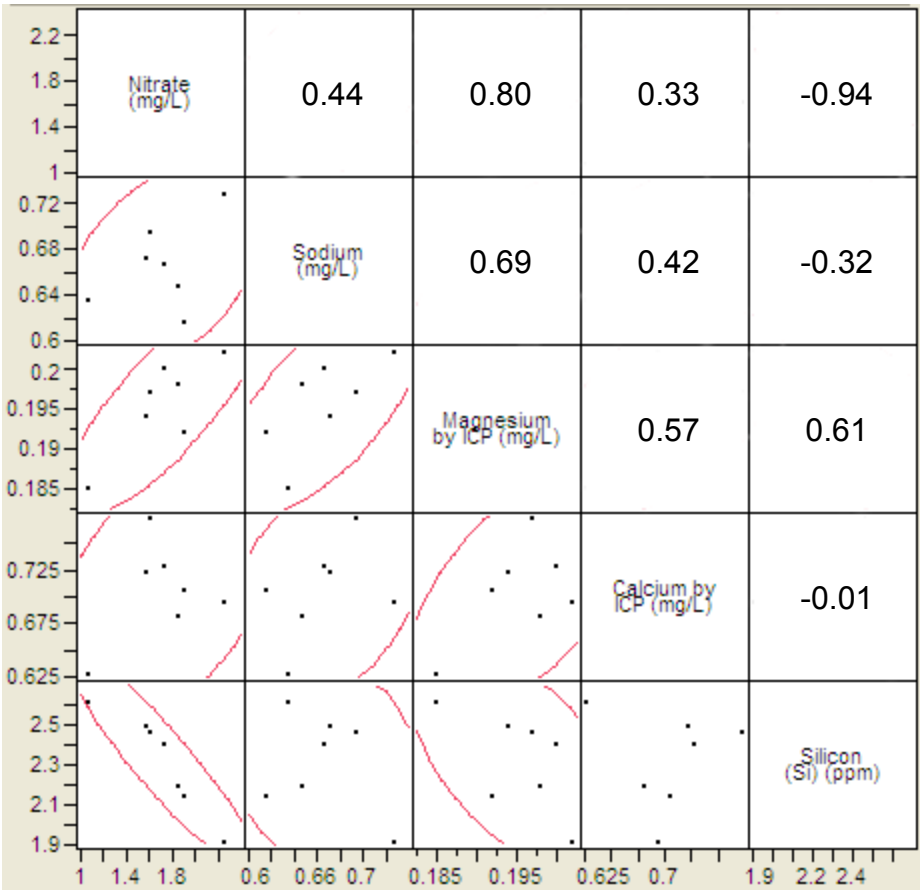
August dataset for Acid deposition ions.



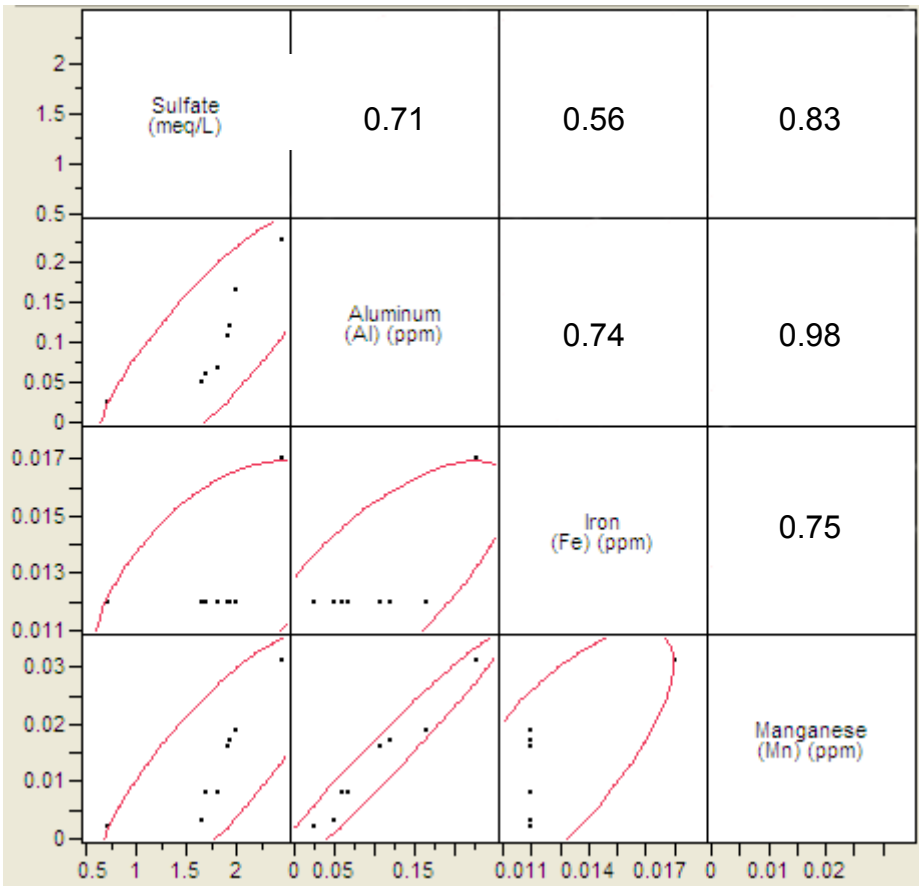
April dataset for Dolomite and Water-Rock ions.



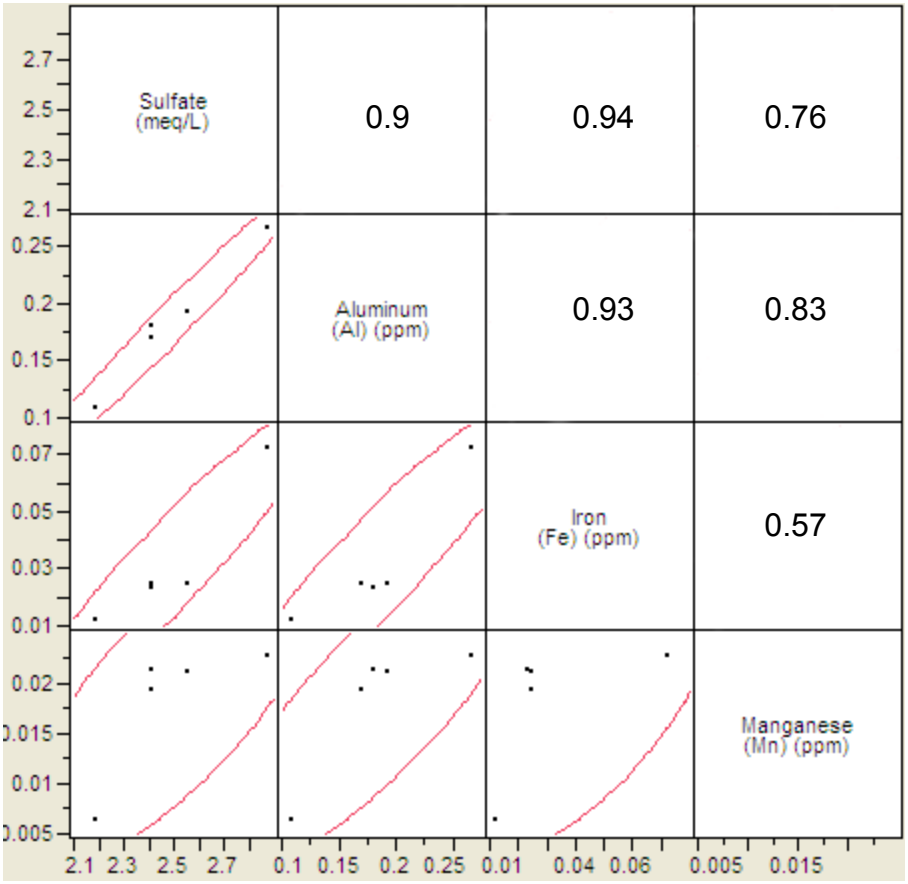
July dataset for Dolomite and Water-Rock ions.



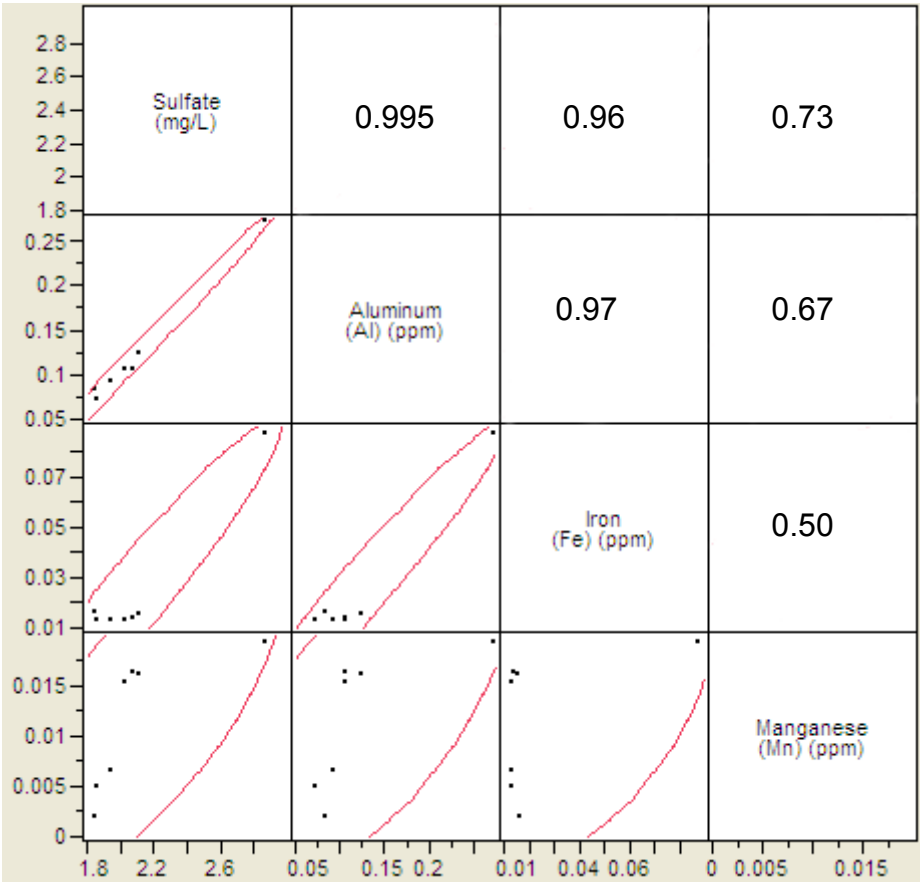
August dataset for Dolomite and Water-Rock ions.



April dataset for Acid Rock Drainage ions.



July dataset for Acid Rock Drainage ions.



August data set for Acid Rock Drainage ions.

Excerpt from QUALITY ASSURANCE PROJECT PLAN for U.S. ENVIRONMENTAL PROTECTION AGENCY

NATURAL RESOURCE POLICY CENTER
THE UNIVERSITY OF TENNESSEE, KNOXVILLE

Project : EFFECTS OF ACIDIC DEPOSITION ON FISH AND WATER QUALITY IN THE GREAT SMOKY MOUNTAINS NATIONAL PARK

DEPT. OF CIVIL & ENVIRONMENTAL ENGINEERING

B.4 Analytical Methods

Chemical analyses were performed at the UTK CEE water quality laboratory. These analyses (and sub-sampling procedures) are detailed in instrument standard operating procedures (Appendices C through E). Water samples were analyzed for the following parameters: conductivity (USEPA Method 150.1), pH (USEPA Method 120.1), ANC (Mantech PC-Titration Plus); sulfate (SO_4^{2-}), nitrate (NO_3^{2-}), ammonium (NH_4^+) chloride (Cl^-) (Dionex IC, Standard Methods 4110); Al, Ca, Cu, Fe, K, Mg, Mn, Na, Si, and Zn (Thermo Electron Intrepid II ICP-AES, vacuum-filtered (0.45-µm) and acidified, USEPA SW-846 Method 6010B). Quality control/ quality assurance samples, in the form of spikes, splits, and replicates, were implemented in each analytical procedure. Ion balances were performed on samples for additional quality assurance.

When samples are brought to the laboratory from the field, they are immediately run on the Man-tech autotitrator to measure pH, ANC and conductivity. Within two weeks, samples are sub-sampled appropriately for IC and ICP analyses. Samples are run on the IC and ICP within 2 weeks of when they were sub-sampled. The maximum turnaround time is 30 days. Instrument logs are maintained for each instrument. When quality control measures do not meet specified criteria in a specific run, the samples are run again. Additionally, when a sample does not maintain less than a 15% ion balance difference, samples are reanalyzed.

In the laboratory whole-body sodium concentrations of trout samples were determined. All trout samples were immediately put in a cold room (4° C) and within one week were oven-dried at 70° C for 5-7 days. Dry mass was determined for all trout sampled. Following the procedure of Grippo *et al*, (1996), dried trout were put into amounts of trace metal grade nitric acid, appropriately diluted with deionized water and vacuum-filtered through 0.45-µm filter for analysis of whole-body sodium concentrations

using an ICP-AES. Whole-body sodium was normalized by dividing by wet mass of trout samples to account for differences in trout mass (Grippo *et al*, 1996).

For 2-3 year-old adults, fish sampled from cages will be euthanized and samples of gill tissues will be immediately collected. gill tissues will be preserved in 10% NBF for histological analyses. Fish gills for histopathology will be excised from the head and processed in paraffin for routine histological examination (Henry and grizzle, 2004). gills will be oriented in the paraffin block such that the filaments will be at a 30 to 40° angle to the plane of the section so that the leading and trailing edges of the filament and lamellae can be examined (Henry *et al*., 2001). Lesions in gill tissues will be recorded and quantified.

Hazardous waste from chemical standards, instrument wastewater, and acidified trout samples are disposed of as specified by UTK hazardous waste management guidelines.

Test America Analytical Testing Corporation performed DOC analyses for selected samples. Sample were acidified, filtered through a 0.45-um filter and measured for total organic carbon.

B.5 Quality Control

All procedures used to chemically analyze water samples are based upon standard published methods (Table 2). 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 analyses are performed.

Table 6: Quality Control Methods.

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
$\delta^{18}O$ *and* δD	Mass Spectrometry	Thermo-Finnigan Delt Plus dual inlet mass spectrometer , Thermo-Finnigan Equilibrator	Gas IRMS, as in Finnigan MAT, Application Flash Report No. 19
Dissolved Organic Carbon (DOC)	Combustion Oxidation	Shimadzu Model 5050 TOC analyzer	EPA Method 415.1

B.5.1 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-mS/cm. Some of the QA\QC samples include; reagent blanks (5%), spikes (5%), and replicates (10%).

The QA/QC of the measurement can be expressed by accuracy and repeatability (Variation in measurements obtained when one person takes multiple measurements using the same instrument and techniques on the same analytes). Accuracy expresses how close a measured value to the "true" value. We use USGS known sample to examine the accuracy. One known USGS check solution will be run for 10% of samples. If the deviation between measured and the "true" value is below 10%, the measurement results for that five samples are acceptable. Otherwise, re-measurement for these samples is required. Repeatability is checked by re-measure one sample for several times. We select two or three samples to determine the repeatability in one batch (~5%).

Detection limit is obtained by measuring diluted standard solution. The standard solution is diluted by two times or five times until no data can be read from the peak. The smallest concentration is the detection limit. This method is appropriate if there is no peak for blank solution. Otherwise, the method from IUPAC is employed to determine detection limit by measuring blank sample for 10 times to calculate by using following equation: Detection Limit = blank sample mean + 3 × standard deviation.

B.5.2 ICP-AES QA\QC Procedures

QA/QC samples are prepared and analyzed to ensure results are precise and accurate. Field and laboratory QA/QC samples will comprise at least 20 % of the samples. A quality control check sample is prepared from the standard stock solution. Using a micro pipette and the micro-balance, add one-ml of the stock to a clean HDPE bottle. Then add 98-mls of DI to bring the total to 99-mls. Using a 1-ml volumetric pipette, add one-ml of ultra pure nitric acid to the QCC. Put recorded amounts of stock solution, DI water and ultra pure nitric acid added to each standard into excel spreadsheet (see appendix) to determine exact concentrations of metals in standards. Approximate standard concentrations are shown in Table 3. The ICP method is set to

run a QCC sample every 12 samples. The software is programmed to ensure the QCC sample gives concentrations within 10% of what is expected (the above concentrations). If the concentration of a particular element is not within 10%, the element is flagged as a failure.

Table 7: ICP QCC Sample Concentrations

Element	QCC (ppm)
Al	.5
Mn	.5
Cu	.5
Zn	.5
Na	.5
K	1
Si	1
Fe	.5
Ca	1
Mg	1

A trace metal sample is obtained from the USGS. The sample must be acidified to 1% with ultra pure nitric acid just as the standards and QCC sample are prepared. The sample is ran every 12 samples. The most probable values for this sample can be obtained from the USGS's Standard Reference Sample website, which can then be compared to the ICP results. Ensure that results are within 10% of the most probable values. This can be problematic with some elements in the trace sample that have concentrations in the low ppb range. During sample preparation, once every 20 samples randomly select one of the prior 20 samples and prepare it as described in Section 2.0. Then label the sample as the laboratory ID number plus the letter S (*e.g*., N123S). The sample is run with the other samples on the ICP. The results for the actual and the split samples can then be compared and should be within 15% of each other. During sample preparation, once every 20 samples randomly select one of the prior 20 samples and prepare it as described in Section 2.0. Then label the sample as the laboratory ID number plus the word Spike (*e.g.*, N123Spike). Using a micro-pipette, add 0.250-mls of the standard stock to the spike sample. The sample is run with the other samples on the ICP. The result for the actual sample is then subtracted from the spike sample and divided by the actual amount of the spike to provide a percent recovery (Table 4). The percent recovery should range from 85% to 115%.

Blanks are prepared from deionized water and acidified to 1% with ultra pure nitric acid. The blank sample is ran once every 24 samples. The results should be checked to ensure blank concentrations are near zero. Minimum detection limits are determined annually. The current detection limits are shown in Table 5. The method to determine

detection limits is as follows: a) run 7 replicates of blank samples twice on two separate days, b) determine the standard deviation for each metal from the 14 blank samples, c) multiply the standard deviation of each metal by 3, this is the minimum detection limit for each metal. The detection limits should be within a factor of 2 from the blue book value stated in Standard Methods for the Examination of Water and Wastewater. If all elements are similarly out of range, there is a sample introduction problem. If one or a few lines are out of range, there is a spectrometer problem.

Table 8: ICP Spike Concentrations

Element	Spike (ppm)
Al	.7
Mn	.7
Cu	.7
Zn	.7
Na	.7
K	1.4
Si	1.4
Fe	.7
Ca	1.4
Mg	1.4

Table 9: 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

B.5.3 Auto-titrator QA\QC Procedures

QA/QC procedures to be used include analyzing pH, conductivity, and ANC (Acid Neutralizing Capacity) of water samples by using Man-Tech Auto-titrator. The detail

operation procedures of titrator are present in Standard Operation Procedure for the Man-Tech Auto-titrator. Sample collection and transfer methods are discussed elsewhere.

One aliquot of ~ 40-ml will be immediately taken from each collected sample upon returning from the field. The auto-titrator uses a peristaltic pump to accurately remove the 25-ml that is used for analysis, with the rest being used for rinsing purposes. Samples will all be analyzed in a temperature-controlled laboratory, which is generally at a standard temperature of 250C. Samples will be allowed to equilibrate to room temperature before analysis. If suspended solids are present in sufficient amounts to clog the suction tube, the samples may be allowed to settle and the supernatant liquid sampled directly (USEPA, 1992). Samples collected from areas of the Park containing limestone bedrock, *i.e.*, Cades Cove, will be placed at the end of the sampling tray to minimized any possible cross contamination.

Calibration Procedure: The auto-titrator instrument will be calibrated each time the instrument is used. The conductivity standard will be placed in position one, followed by the two pH buffers (4 and 7), pH/conductivity check, reagent blank and the ANC check sample. A detailed description on auto-titrator set-up protocols can be found in the Standard Operation Procedure for the Man-Tech Auto-titrator.

Standards and Check Samples Defined: Conductivity Standard 500 µs/cm conductivity standard is purchased from Fisher Scientific.

*pH Standard*s: The pH buffer solutions will be purchased from Fisher Scientific. A two point calibration procedure will be used for calibrating the pH probe. Currently, pH buffers 4 and 7 are used for our samples. If samples fall outside the calibration ranges, the instrument will be re-calibrated using the appropriate standards.

Hydrochloric Acid: The 0.01 N HCl acid solution that is used as the titrant will be purchased from Fisher Scientific. Normal range for the acid is 0.0099~0.0101 N. The normality of hydrochloric acid will be standardized by using THAM according to the standard manual titration method from EPA, once the measurement results are abnormal.

pH Probe Filling Solution: The filling solution for the pH probe is a 4 M KCL which will be purchased from Man-Tech Company. The pH probe solution level will be checked prior to use. A pipette is used to fill the probe with the KCL solution if necessary.

pH Probe Storage Solution: The pH storage solution will be purchased from Fisher Scientific. The pH probe can be stored in pH 4 buffer solutions for shorter periods of inactivity.

ANC Check Sample: The ANC check solution will be prepared periodically from NaHCO3. About 1g anhydrous NaHCO3 powder is dried in a desiccator for three days before it is used to prepare the check sample. Dissolve 0.84 g of dried NaHCO3 in 1000-ml of D.I. water. Add the NaHCO3 and then bring the volume up to 1000-ml in a volumetric flask. This concentrated stock solution will contain 500-ppm alkalinity as CaCO3. This 500-ppm solution should be made once every two months. To prepare the final check solution pipette 6-ml of the stock solution with a volumetric pipette and bring the total volume up to 1 L using D.I. water in a 1000-ml volumetric flask, this will yield an ANC check solution of 3-ppm as CaCO3. In following text, ANC check sample refers to this 3-ppm solution. The lifetime of this 3-ppm check sample is 2 weeks.

pH/Conductivity Check Sample: pH 5 buffer solution is used as the pH/conductivity check sample for QA/QC control, just like ANC check sample.

QA/QC Section: The Man-Tech auto-titrator has been in service since August of 2002. In September of 2002, the measurements for pH and conductivity sent into the USGS's analytical evaluation program received "excellent" and "good" scores for those two parameters, respectively. To insure high quality work continues during the operation of the auto-titrator the following QA/QC samples will be analyzed during the use of the instrument.

Analysis Schedule: After every 20 samples an ANC check sample and the pH/conductivity check sample will be run to determine instrumental drift. If any of the check samples are outside the predetermined control limits, the instrument will be re-calibrated and the suspect analysis reran.

Blanks: One D.I. water blank is placed in the position following the pH/conductivity solution. This is to prevent the highly concentrated buffer from contaminating the subsequent sample. There are also field blanks currently being sampled in the Park Wide Stream Monitoring efforts. These QA/QC samples provide a way to test bottle and/or sample cup contamination.

pH/Conductivity Check Sample: The QA/QC limits for the pH/conductivity check sample will follow the recommended guidelines found in Standard Methods (1998) and EPA approved methods. The QA/QC limits specified in Standard Methods for pH are +/- 0.1 pH units from a predetermined value, so the range of pH should be 4.9~5.1. The QA/QC limits approved by the EPA for conductivity are +/-2% of a 100-mS/cm measurement. The averaged conductivity of pH 5 buffer solutions is 5.45ms/cm. It means the conductivity range of pH 5 buffer solution is 5.34~5.56-mS/cm. Therefore, if the pH or conductivity values for the check sample fall outside these predetermined ranges (4.9-5.1 for pH, 5.34-5.56 for conductivity), the source of the discrepancy will be investigated and the samples reran.

ANC Check Sample: The expected value for the ANC check sample is 3.00-ppm as CaCO3. Once a new bottle of ANC check sample is made, that sample should be run for 7 times to get the ranges of conductivity, pH and ANC for the check sample. The quality control limit of +/- three standard deviations will serve the upper and lower control levels. If the ANC check samples fall outside this range, the acid lines for the titration system will be flushed, and the samples will be re-analyzed. If re-run cannot solve the problem, a manual titration of the ANC check sample according to USEPA Method 2320 is required. The ANC and pH from manual titration is compared with the measurement results from auto-titrator to check if the auto-titrator measurement is correct.

Replicates: One randomly re-poured sample will be analyzed during the course of a run. If results from the two samples differ by more than 20%, the source of the discrepancy will be evaluated and the samples possibly reran depending on the findings.

pH Slope and R-square Values: The Man-Tech auto-titrator's software has an automated internal pH slope and correlation coefficient values for QA/QC tracking controls. These automated control charts will be compared to previous values to check if the pH probe is too old so that a new one is needed to replace. The normal lifetime of a pH probe is half a year.

Data Processing: The results of the auto-titrator are exported to excel spreadsheets corresponding to the project associated with those samples. All relevant QA/QC data generated during the run will also be placed in the associated files. No data can be changed without approval after this point. Any corrections to data values will be noted within the spreadsheet along with the reason.

Data Storage: All results are saved in the computer connected to the titrator. In addition, the data should be backed up monthly to store in another computer in another room. The software of that titrator machine also should be backed up once every two months to another computer.

Personnel and Training: One special person is appointed to be responsible for the QA/QC of autotitrator. That person is responsible to draft the QA/QC file, train every user, make any changes in the software, maintain the mechanical parts, make the standard ANC check sample, collect all measurement data to make the statistics analysis, and any other things related to QA/QC. Every time the setting of the machine is changed, all users will be trained to accommodate the new setting. Every new user must take the training before he/she starts to use the machine.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance

Field equipment, including sondes, sonde cases, solar panels, samplers (volume and depth calibration), throughfall/precipitation buckets, tubing, cables, 12-V batteries (voltage), hobo precipitation tipping buckets and data loggers are inspected on every field visit and maintained to manufacturers' specifications. The sonde should be checked for physical damage every visit. Any dirt build up should also be cleaned off of the probes. Sondes are calibrated monthly for 2-point pH, conductivity, 2-point turbidity, and depth according to YSI specification. Water samplers are programmed and calibrated for sample volume, pump mechanics, distributor-arm mechanics, time and date after each capture event. Additionally, communication between sonde and sampler is ensured.

All laboratory instruments are maintained regularly according to manufactures' specifications by instrument operators. New standards are prepared according to Standard Methods, and new standards are run on each instrument during each run to ensure acceptable curve/results.

Relevant Chemical Equations Sheet:

Quartz:

$$SiO_{2(quartz)} + 2H_2O = H_4SiO_{4(aq)}$$

K- Feldspar:

$$3KAlSi_3O_8 + 2H^+ + 12H_2O \rightarrow KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6H_4SiO_4$$

Muscovite

Plagioclase:

$$NaCaAlSiO_8 + CO_2 + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + Na^+ + Ca^{2+} + HCO_3 + SiO_{2(aq)}$$

Dolomite:

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$$

Acid Mine Drainage:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 4Fe^{3+} + 8SO_4^{2-} + 4H^+$$

The concentrated acid can liberate toxic heavy metals from their ores. (secondary sulfate)

Nitrate:

$$NH_4^+ + 3H_2O \leftrightarrow NO_3^- + 10H^+ + 8e^-$$

Denitrification:

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O$$

VITA

Candice Owen grew up in Carthage, Tennessee, a small town outside of Nashville, TN. She graduated from Smith County High School. Candice received her Bachelor of Science degree in Civil Engineering from the University of Tennessee, Knoxville. She received her Master of Science in Environmental Engineering in 2007.