To the Graduate Council:

I am submitting herewith a thesis written by James Chadwick Roby entitled "Water Quality Characterization, Stormwater Analyses, and Statistical Modeling of Stream Water Quality in the Little Pigeon River Watershed of the Great Smoky Mountains National Park." 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.

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Water Quality Characterization, Stormwater Analyses, and Statistical Modeling of Stream Water Quality in the Little Pigeon River Watershed of the Great Smoky Mountains National Park

A Thesis
Presented for the
Master of Science
Degree
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James Chadwick Roby
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Abstract

Scheduled road construction prompted intensive water quality monitoring of the adjacent stream, the Little Pigeon River. Three phases of monitoring was planned to fully assess any impacts construction may have: pre, during, and post construction monitoring. One year of pre-construction monitoring has been completed. Three monitoring sites were installed. Site 1 was below, Site 2 in the middle, and Site 3 above all road construction. Each site had a YSI sonde that measured 15-minute pH, turbidity, conductivity, temperature, and stage. Storm samples were also captured through use of an Isco auto-sampler. Additionally, bi-weekly grab samples were taken at each site. All collected storm and grab samples were measured for pH, conductivity, acid neutralizing capacity, chloride, nitrate, sulfate, and ten metals including aluminum. In addition to the three main stream sites, Site 4 was located on Ramsey Prong in the south-east side of the watershed. It contained a YSI sonde that measured 15-minute pH, conductivity, temperature, and stage. Four grab samples were taken during base flow at Site 4. Two precipitation stations were also operated that contained bulk and sequential precipitation collectors in addition to tipping bucket rain gauges.

Acid deposition is a major water quality driving force. pH and acid neutralizing capacity (ANC) are often used as indicators of acid deposition effects during base and storm flow. Descriptive statistics of sonde and base flow grab sample stream indicates acceptable base flow stream pH for Sites 1 – 3. However, Site 4 mean stream pH of 5.76 indicates unsuitable conditions for aquatic ecosystems. Sonde data and storm samples showed numerous occasions of episodic acidification at Sites 1 – 4 when using stream pH 5.5 as the criteria for acidity (Lachance and Bobee 1991). Similar to pH, base flow ANC

was acceptable at Sites 1 and 2. However, Sites 3 and 4 mean base flow ANC indicated high sensitivity to acid deposition. Site 4 was likely affected by acid deposition but Anakeesta geology is also believed to play a role in the depressed stream pH and ANC.

Increased stream concentrations of aluminum, sulfate, and nitrate are also indicators of acid deposition impacts. Mean stream aluminum, sulfate, and nitrate concentrations increased 25 to 59%, 12 to 24%, and 33 to 39%, respectively compared to base flow concentrations. Notably, mean concentrations of sulfate and nitrate found in precipitation samples were comparable to mean concentrations observed during storm flow. Mean concentrations of aluminum found in precipitation are not comparable to base or storm flow stream concentrations. This indicates soil leaching of aluminum caused from acid deposition.

Using EPA criteria, numerous occasions of metal exceedances occurred during base and storm flow at Sites 1 – 3. Data for calcium and magnesium indicates low hardness during base and storm flow. This exacerbates problems associated with metal toxicity. Exceedances increased during storm flow as expected. Metal exceedance of EPA criteria for aluminum, copper, and zinc endured for at least 20.75 hours during a storm event on July, 25, 2004. However, several studies showed that metals concentrations must exceed EPA criteria by three fold to reach lethal concentrations that kill 50% (LC50) of brook and bull trout (Kazalauskiene et al. 2003 and Hansen et al. 2001.) LPR exceedances were not as severe and the duration for the LC50 values were also longer than observed continuous metal exceedances in the LPR.

Turbidity and pH are perhaps two of the most commonly measured stream water quality parameters due to their overall importance on aquatic ecosystems. A large

quantity of sonde pH and turbidity was collected during this study. The data were used throughout this document to describe pH and turbidity. Multiple linear regression models were also constructed using sonde data. Storm event data were isolated to build a storm event pH and turbidity multiple linear regression models. Ultimately, lagged stage, sine and cosine functions of the day fraction, and total rain volume were used to predict storm event pH. Similarly, stage, stage^2, stage intensity, and sine and cosine functions of the year fraction were used to predict storm event turbidity. Both models had several deficiencies that possibly prevented the best possible linear regression parameters from being estimated. Error residuals were not normally distributed and were serially correlated. However, high r^2 values and application to a validation storm event data set showed the models were able to reasonably predict storm event pH and turbidity.

The developed storm event linear regression models for pH and turbidity serve several purposes. The models show association between the response and predictor variables. From the associations developed causes for increased turbidity and decreased pH may be inferred (i.e. precipitation input depresses pH and increases turbidity). Additionally, a major objective was to form a basis of comparison of pre, during, and post construction water quality. In order to do this major water quality drivers must be understood in order to fully assess construction impacts. An understanding is particularly important for storm events because mean or median base flow water quality can be compared for pre, during, and post construction, comparing mean or median storm events is likely to be very misleading. The uniqueness of each storm event and the relative infrequency of significant storm events can cause mean or median to be misleading. Regression models allow the water quality to essentially be normalized for the size of the

storm event and seasonal and diel patterns. The developed preconstruction storm event models should fit the during and post construction water quality. If not, construction impacts can be inferred.

As stated above, a major objective was to form a basis of comparison for water quality during the various stages of this study. Once data from other phases of this study have been collected independent comparisons from the water quality sites may be completed. With these data it was prudent to first establish that the three main stream sites' water quality were significantly different. Sonde and base flow pH was chosen to ascertain significant differences between stream sites. All sites had significantly different sonde and base flow pH with one exception. Mean base flow pH at Sites 1 and 2 were not found to differ significantly.

A number of interesting water quality attributes were noticed during this study. Sonde base flow pH, temperature, and dissolved oxygen exhibited distinct diel cycles. Temperature and dissolved oxygen were caused by air temperature variation. Interestingly, pH diel cycles are believed to be due to biological photosynthesis and respiration. A slight diel cycle in conductivity also corresponded to biological action. Another unexpected water quality attribute was upward pH spikes at the onset of storm events. A 2.07 unit increase in pH was observed at Site 1 in response to a storm event on September 3, 2003. However, increases were generally one pH unit in magnitude. Examination of storm event water quality data showed these pH increases were due to increased stream alkalinity. Precipitation also showed similar alkalinity increases which indicate antecedent accumulation in the watershed of alkalinity from an unknown source.

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Chapter I. Introduction

1. The Little Pigeon River Watershed Construction Monitoring Study

The Little Pigeon River (LPR) watershed is located on the northeast side of the Great Smoky Mountains National Park (GRSM). The one mile paved portion of the Greenbrier road in the watershed will be reconstructed and widened. The current road is a narrow two lane paved road with many potholes. South of this major construction will be minor construction areas that will most likely have little effect on water quality. The start and end date of the construction has not been determined but is expected to begin in the fall of 2005.

A primary goal of the National Park Service (NPS) is to preserve the natural environment for which it has jurisdiction over. The NPS is concerned that the road construction have no long term impacts on the adjacent Little Pigeon River which is designated as an Outstanding National Resource Water (ORNW). Consequently, the NPS required that the Little Pigeon River be monitored before, during, and after construction. This document is a synthesis of the preconstruction period and will cover data collected from June 23, 2003 to September 29, 2004.

2. Purpose of Study

The main purpose of this study was to form a basis of comparison for the construction and post construction water quality. Multiple sections will cover several statistical methods to form a basis of comparison for future water quality collected. Another purpose was to characterize water quality and to investigate the major driving forces of water quality in the watershed particularly during storm events which are

believed to result in the worst water quality. Graphical and statistical models will be used to ascertain the important water quality driving forces. Several statistical models were developed to predict water quality as a function of actual water quality driving variables.

3. Objectives

The objectives of this study were to:

- Statistically characterize water quality data collected during the preconstruction phase for comparison to construction and post construction water quality and to further the understanding of water quality variables
- Develop multiple linear regression models that can be used to infer drivers of water quality and be applied to assess changes in construction and post construction water quality.
- Evaluate whether acid deposition/precipitation is a major driving force of stream water quality through statistical methods and mass balances.
- Identify which ion(s) have the most influence on ANC change and consequently pH change
- Assess how ions vary during a storm event.
- Determine metal exceedances based on EPA guidelines

Chapter II. Review of the Literature

1. Introduction

The primary focus of this study was to monitor water quality in the Little Pigeon River before construction in order to form a basis of comparison for during and post road construction water quality to determine if any environmental impacts were caused by construction. This requires understanding other impacts on water quality especially during storm events when construction site runoff has potential to result in the greatest effect on water quality. The literature review below discusses acid deposition effects on water quality because acid deposition is arguably the greatest confounding factor in deciding which adverse impacts were caused by construction and which by other phenomena. Additionally, several other water quality factors will be discussed. Although construction impacts are discussed briefly in this literature review, a more detailed literature review will be performed in the next phase of monitoring, i.e., during construction, that discusses in more detail sediment, suspended solids and turbidity from natural and construction sources.

2. Acid Deposition

Atmospheric acid deposition can be detrimental to stream water quality. Acid deposition (dry and wet) is composed primarily of anthropogenic sources of sulfuric and nitric acids and ammonium (Driscoll et al. 2003). Acid deposition has been studied for decades and is largely attributed to the burning of fossil fuels. Sulfur and nitrogen compounds are released into the atmosphere where they are oxidized into sulfuric and nitric acids. This input of acid lowers the pH of rain resulting in "acid rain" and increases

the concentration of sulfate and nitrate in precipitation. Strong positive correlations have been made between sources of sulfur dioxide and sulfate in wet deposition (Driscoll et al. 2003). It follows that high levels of sulfate is an indicator of acid deposition. Acid deposition can impact an ecosystem in a variety of manners. Acid deposition can cause:

1. Soil leaching of base cations and aluminum
2. Depressed stream pH and ANC (acid neutralizing capacity)

(Driscoll et al. 2003)

Leaching base cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) from soils robs plants of necessary nutrients. Once base cations have been displaced aluminum becomes easier to leach. Depressed pH, increased aluminum and other metals can also be harmful to aquatic ecosystems. These factors will be discussed in future sections.

In recent years focus has turned to understanding the chemical dynamics of episodic acidification (DeWalle et al. 1994). Rearranging a charge balance equates ANC change to changes in cations and other anions:

$$ANC = (\text{Base cations} + NH_4^{+} + Al^{n+} + \text{other cations}) - (SO_4^{2-} + NO_3^{-} + Cl^{-} + \text{other anions})$$

Equation 2-1

From Equation 2-1 it can be shown that processes that decrease cations or increase anions result in a decrease in ANC (DeWalle et al. 1994). A number of authors have related changes in base cations, sulfate, and nitrate as causes of acidic deposition (DeWalle et al. 1994, Herlihy et al. 1993, and Schaefer et al. 1990). However, it is unclear why changes in these ions by themselves are equated to a cause of episodic acidification. For example, sulfate ions are relatively un-reactive and do not cause depressed stream pH. It can be inferred that sulfate and nitrate dominated ANC changes are due to acid deposition.

From this context sulfate is a symptom of acid deposition but not the cause. Acid deposition causes soil leaching which increases base cation concentrations. It follows that ANC changes dominated by base cation dilution could not be attributed to atmospheric acid deposition but rather due to simple dilution with precipitation (Schaefer et al. 1990). If ANC changes are dominated by simple dilution of stream water then reducing acid deposition may improve baseline ANC but may only marginally improve episodic ANC (Schaefer et al. 1990).

Aluminum, though toxic to aquatic ecosystems at sufficient levels, has been identified as a pH buffer (DeWalle et al. 1994 and Schaefer et al. 1990). The process is unclear but may be due to hydrogen ions exchanging with aluminum in soil sources thus reducing the total hydrogen input. However, this effect is only temporary and the hydrogen ions are eventually displaced. This later displacement could be a source for chronic acidification.

3. Effects of pH and Metals on Trout

Brook trout are the only native trout found in the GRSM. Brook trout were once widespread but are now only found in elevations above 3,500 feet (GSMNHA and NPS 2001). Brook trout were once found throughout the LPR watershed but are now only found in high elevation of the southeast side of the watershed (GSMNHA and NPS 2001). Due to the brook trout's limited range the National Park Service is especially attentive of acidification and water quality impacts where brook trout are known to inhabit.

There are many factors that can contribute to a decline of trout including acidification, loss of habitat, migration barriers, and competition with non-native species

(Hansen et al. 2001). Barnett (2003) presented a comprehensive discussion of the effects of aluminum and pH on rainbow, brown, and brook trout. Some of his findings will be briefly discussed. Fish can suffer multiple effects of acute and chronic acidification. Effects range from avoidance of particular areas, reduced size, and death of adult and eggs. It was found that waters with low calcium concentrations can also be detrimental to trout since sufficient levels of calcium have been shown to help offset acidification. Fish subjected to chronic acidification were less tolerant of an acute lethal dose of acidification. This makes trout in stream waters plagued by chronic acidification more susceptible to episodic acidification commonly encountered in the GRSM. Aluminum as free ions has been shown to be toxic to aquatic organisms. The solubility of aluminum increases as pH decreases thus adding to the damaging effects of acidification. A summary of Barnett's (2003) findings on pH effect are shown in Table 2-1.

Hansen et al. (2001) studied the toxicity of cadmium and zinc with varying hardness levels. This study used bull and rainbow trout. The bull trout is not found in the GRSM but will still be included in this discussion to give some indication of variability among trout species. The lethal concentration at which 50% of the species are killed (120hr -LC50) for cadmium ranged from 0.51 μg/l to 5.23 μg/l and 0.35 μg/l to 2.07 μg/l for bull and rainbow trout respectively depending on pH and water hardness (Hansen et al. 2001). LC50 for zinc ranged from 30.1 μg/l to 395 μg/l and 23.9 μg/l to 257 μg/l for bull and rainbow respectively (Hansen et al. 2001). For all treatment groups except one, the LC50 was higher for bull trout compared to rainbow trout (Hansen et al. 2001). Hardness was found to have an inverse relationship with metal toxicity. A six-fold decrease in cadmium toxicity and a three to ten fold decrease in zinc toxicity with a

Table 2-1. Summary of effect pH values have on trout (Barnett 2003).

pH Range	Effects
7.0 - 6.0	Unlikely to be harmful.
6.0 - 5.0	Likely to be harmful to trout when aluminum concentrations exceed 0.2 mg/l. Lower part of range may be harmful to eggs, fry, and non-acclimated trout if calcium, sodium, and chloride concentrations are low.
5 - 4.5	Likely to be harmful to eggs and fry, and to adults in soft water containing low concentrations of sodium, calcium, and chloride. Reduced production, reduced growth, and abnormal behavioral patterns are likely in this range. Aluminum concentrations increase the negative effects.
4.5 - 4.0	Likely that trout could not survive in this range for prolonged periods of time. Reproduction in this range severely limited.
4.0 - 3.5	Likely to be acutely lethal to all salmonids.

three-fold increase in hardness were observed for both species (Hansen et al. 2001). Sufficient levels of hardness can reduce the toxicity effects of zinc and cadmium in low pH waters. This is important since park waters tend to have low hardness levels making trout populations more susceptible to metal toxicity.

Hansen et al. (2001) also compared combined toxicity of zinc and cadmium. It was found that bull trout were less resistant with both metals present but not rainbow trout. Kazalauskiene et al. (2003) found that a mixture of copper, zinc, nickel, chromium, and iron did have a partial additive effect on rainbow trout. These effects were multiplied in fish larvae and embryos (Kazalauskiene et al. 2003). Additionally, younger fish were found to be less sensitive to metal toxicity than older fish. It was also found that increased temperature lowered the LC50 values (Hansen et al. 2001). A summary of the two studies is shown in Table 2-2. Zinc LC50 was much higher for rainbow trout in the Kazalauskiene et al. (2003) study. However, hardness was almost three times higher and time exposure was less.

Table 2-2. Comparison of rainbow trout LC50 for metal toxicity.

Study	LC50	Copper µg/l	Zinc µg/l	Iron µg/l	Nickel µg/l	Cadmium µg/l	Hardness mg/l	pH
Hansen et al. 2001	120- hr	**	23.9 - 257	**	**	0.35 - 2.07	30 - 90	6.5 - 7.5
Kazalauskiene et al. 2003	96-hr	700	3800	39000	19300	**	284	7.8 - 8.1

**Not tested.

4. Metals Criteria for Aluminum, Copper, and Zinc

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:

$$\text{CMC (dissolved)} = \exp\{m_A [\ln(\text{hardness}) + b_A\}\ (\text{CF}) \qquad \text{Equation 2-2}$$

$$\text{CCC (dissolved)} = \exp\{m_C [\ln(\text{hardness}) + b_C\}\ (\text{CF}) \qquad \text{Equation 2-3}$$

Where:
m_A, m_C, b_A, and b_C = parameters found from toxicity data
hardness = water hardness in mg/l as $CaCO_3$
CF = conversion factor for converting from total recoverable metal to dissolved metal

The parameters listed in Table 2-3 were established for copper and zinc for the above equations. Typically the range for hardness is less than 5 mg/l as $CaCO_3$ for the waters of the Great Smoky Mountains National Park. For low hardness waters like these, the metal toxicity predicted by the above equations is fairly low such that there could be a significant number of exceedances. Table 2-4 displays criterion concentrations for hardness levels of 1,5,10, and 20 mg/l.

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 $CaCO_3$. 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).

The ability to extrapolate criterion concentration values for such low values of hardness still remains questionable. 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). If there are site-specific questions about the applicability of the 2002 Criteria, then the EPA suggests two alternative procedures. The first procedure involves forming a Water Effect Ratio (WER) for each metal of interest. The second procedure only applies to copper and involves using a biotic ligand model (BLM).

Water Effect Ratio (WER) is an EPA software program used to derive site specific water quality criteria and is a companion to the Water Quality Standards and Criteria software. In order to make use of this software, toxicity tests must be performed

Table 2-3. 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

Table 2-4. Water quality criteria for hardness-dependent metals.

Hardness	Copper		Zinc	
mg/l as $CaCO_3$	CMC (dissolved) µg/l	CMC (dissolved) µg/l	CMC (dissolved) µg/l	CMC (dissolved) µg/l
1	0.175	0.175	2.367	2.387
5	0.799	0.692	9.257	9.338
10	1.535	1.252	16.655	16.803
20	2.950	2.264	29.965	30.238

on two side by side dilution waters (site water and blank). By comparing the tests results of the two dilution waters, a WER is determined for each metal of concern. This WER is then multiplied by any applicable state or national water quality criteria in order to obtain a site specific value. Due to the demands of toxicity testing, the WER option would not be cost effective for the Great Smoky Mountains National Park projects.

The second procedure, biotic ligand model (BLM) was recently proposed in the EPA 2003 Draft Update of Ambient Water Quality Criteria for copper (USEPA 2003). Unlike the previous empirical relationships of toxicity, BLM accounts for individual water quality variables not just hardness. The basic concept behind this method is that toxicity is related to metal bound to a biochemical site (biotic ligand) and binding is related to total dissolved metal concentrations and complexing ligands in water (USEPA 2003). The biotic ligand model incorporates metal speciation reactions and organism reactions. The necessary input parameters for the model are: pH, dissolved organic carbon, percent humic acid, temperature, major cations, major anions, dissolved inorganic carbon and sulfide. Although this model does present a significant improvement over previous hardness dependent equations, it is not a viable option for the Great Smoky Mountains National Park projects due to a lack of data required as input parameters.

The EPA 2002 Water Quality Criteria should be applied to the waters of the Great Smoky Mountains National Park since available toxicity data for copper and zinc at hardness levels less than 20 mg/l are quite limited and the WER and BLM procedures are not viable options. It is still unclear as to whether applying hardness-dependent formulas below the range at which they were developed is problematic. 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 $CaCO_3$.

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 exceedence frequency of once every three years was appropriate.

5. Turbidity Effects on Fish

Turbidity is a measurement of light scattered and absorbed due to the presence of particles in water and is often used as a surrogate for suspended solids measurement. Higher turbidity readings generally mean higher suspended solids are present. Increased suspended solids can cause reduced fish diversity and alter size, age structure, and species composition (Vondracek et al. 2003). Excessive suspended solids can also result in "avoidance behavior, impaired respiration, reduced feeding rates and growth, reduced tolerance to disease or toxicants, increased physiological stress, and mortality" (Vondracek et al. 2003). The ill effects of suspended solids may be caused by:

1. Acting freely on free swimming fish
2. Preventing the successful development of fish eggs
3. Modifying the natural movements of fish

4. Reducing availability of food
5. Habitat alteration

The cause of number four can be a number of mechanisms. For example, a relationship has been shown between cloudiness of water and a fish's ability to see prey. Brook trout were found to react to prey at 30 cm in water with turbidity of 1 NTU. In water with turbidity of 40 NTU the reaction distance was reduced to less than 10 cm (Newcombe 2003). In general, as turbidity increases, fish reaction to prey is reduced.

There is little debate that increased suspended solids adversely affect aquatic ecosystems. The difficulty arises in setting a standard for exceedence. The Minnesota Pollution Control Agency proposed setting a general turbidity exceedence for streams at 25 NTU (Vondracek et al. 2003). General standards are applied that affects all aquatic life, but different species have varying tolerance levels. A general standard also does not take into account that different levels of turbidity can have little or no effect depending on the time exposure. Research has shown that fish can tolerate high levels of turbidity for short duration better than prolonged mid-ranged turbidity levels (Newcombe 2003). Figure 2-1 is a generic model of turbidity level, duration, and effects on fish but clearly illustrates the point that prolonged mid-ranged turbidity levels can be as lethal as high short duration turbidity exposures. Newcombe (2003) developed a visual clarity model that gauges the ill effects of turbidity. The model relates turbidity levels with duration and results in a magnitude of ill effect. Higher model results correlate to a greater negative effect. Work in this direction may result in more appropriate turbidity standards.

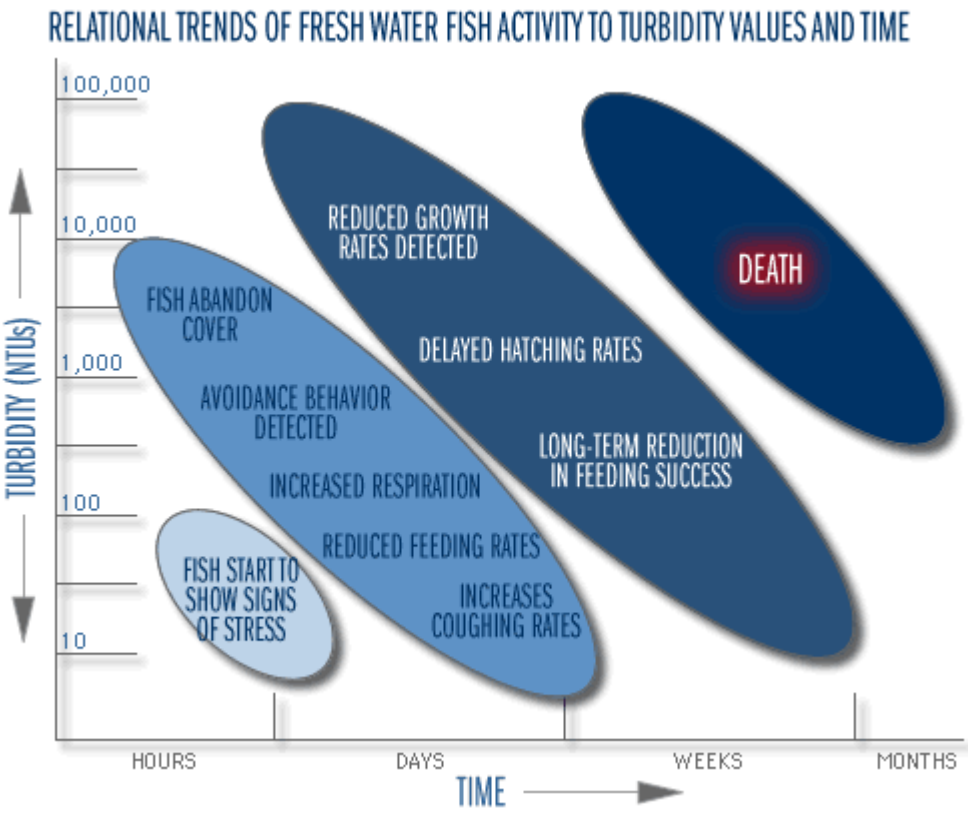

Figure 2-1. Turbidity vs. time: general effects on fish.
(http://waterontheweb.org/under/waterquality/turbidity.html)
(Schematic adapted from "Turbidity: A Water Quality Measure", Water Action Volunteers, Monitoring Fact sheet Series, UW-Extension, Environmental Resources Center. It is a generic, un-calibrated impact assessment model based on Newcombe, C. P., and J. O. T. Jensen. 1996. Channel suspended sediment and fisheries: a synthesis for quantitative assessment of risk and impact. North American Journal of Fisheries Management. 16: 693-727.)

6. Water Quality Effects on Macroinvertebrate Communities

Macroinvertebrates are an excellent indicator of water quality since they are sensitive to changes in the ecosystem and cannot easily escape changes in water quality. Courtney and Clements (2003) used stream microcosms to determine response of macroinvertebrates when exposed to acidic conditions for seven days. Four groups were used that had target pH values of 7.4, 6.5, 5.5, and 4.0. Only the pH 4 group had a significant decrease in the total number of individuals remaining. The total remaining was measured by the number of individuals that drifted downstream. Not all were dead but were still counted in the decreased total number. The drift of living organisms suggests a negative response to acidification. Additionally, the researchers noticed immediate negative behavior change in the pH 4 group which indicates a negative response to episodic acidification. Stream pH of 4 is rarely encountered in the GRSM but has been observed during episodic events. Survival rates also varied between species but only significantly varied in the pH 4 group (Courtney and Clements 2003).

As with fish, macroinvertebrate are also affected by metal toxicity. The effect of heavy metals (Cd, Cu, and Zn) at CCC levels resulted in varying responses by macroinvertebrate (Courtney and Clements 2003). Some species responded more adversely to acidic conditions than chronic heavy metal exposure while others more adversely to heavy metal exposure. The combined affect was greater for all species. There are several suspected mechanisms believed to be at work in acid and metal toxicity. Metals may be transported across membranes by ion pumps thus processes that increase ion concentration (e.g. increased hydrogen and metal concentration) will generally have negative effects on macroinvertebrates (Courtney and Clements 2003).

A study of Swiss Alpine streams found similar results to the previous discussed study (Lepori et al. 2003). The Swiss study used principal components to group streams based on water chemistry. The groups were then compared for differences in macroinvertebrates. Streams that were acid sensitive had different macroinvertebrate populations than that of highly buffered streams. Diversity was also lowest in acid sensitive streams. Differences in macroinvertebrate were also found in streams that had similar base flow chemistry but different varying episodic chemistry (Lepori et al. 2003). This indicates that storm flow chemistry is needed to fully assess the health of a stream.

7. Potential Environmental Impacts of Road Construction

There are a number of potential sources for pollution in storm run-off including road construction, urban areas, industry, and agriculture activities among others. Fortunately the LPR watershed run-off has limited sources from which to wash pollutants into the receiving streams. This means that road construction impacts may be easier to distinguish but has potential to elevate pollutant loads considerably.

A monitoring program began in April 1991 that ceased monitoring in June 1997 for I-181 highway expansion in Erwin, TN that began in 1990 and completed in 1996 (Holt et al. 2003). The study used a variety of techniques to determine impacts that construction activities had which included water quality measurements, habitat assessment, and fish counts. Unlike the LPR study, data prior to the start of construction was not available. For comparison purposes control sites with similar attributes were selected. Habitat assessments were significantly lower for construction sites compared to the control sites. Water quality parameters were significantly higher for all the seven constituents measured at the water quality sites. Over a five fold increase in mean

suspended solids was noted. An increase in alkalinity and hardness were among the significant increases observed. For the LPR this would not be detrimental since increased hardness tends to buffer against metal toxicity and alkalinity against episodic acidification. Fish populations were not found to be significantly different. Overall, the constructions activities were shown to have impacted the water body, and although fish communities did not seem to suffer, long-term water quality degradation was apparent (Holt et al. 2003).

Contrasting with the Holt et al. (2003), a different study found that although suspended solids increased five fold during construction of a freeway in Travis County, TX, preconstruction levels were attained after construction activities ceased (Barrett et al. 1997). The same study also found that turbidity increased 1100% when comparing results for upstream and downstream of construction (Barrett et al. 1997). Additionally, some pollutants were actually found to decrease during construction activities primarily due to reduced traffic pollution. Overall, construction activities were found not to have a long term impact on water quality (Barrett et al. 1997).

Numerous road construction projects have been completed in the GRSM with mixed results. A road project in 1963 resulted in a reach being permanently devoid of fish (Huckabee et al. 1975). Water quality was degraded by continuous leaching from road fill that contained sulfide materials. Upstream of the fill pH ranged from 6.5 to 7.0 while downstream it ranged from 4.5 to 5.9. Alkalinity was also lower downstream (Huckabee et al. 1975). Monitoring results for two tunnel projects near Walker Camp Prong and West Prong Little Pigeon River in the park found no statistically identifiable impacts as a result of construction. Partially this was attributed to the small area

contribution the construction site had on the watershed (Hedrick 2002). Barring exposing harmful geology, increased suspended solids will potentially have the most impact on aquatic life in the Little Pigeon River during construction.

8. Diel Cycles

Merriam-Webster Online Dictionary defines diel as "involving a 24-hour period that usually includes a day and the adjoining night." A diel cycle as applied to this research is the oscillating increase and decrease of water chemistry. This is also referred to as a diurnal-nocturnal cycle. Diel cycles can be seen in a variety of stream water chemistry such as pH, temperature, metals, and dissolved oxygen. A diel cycle is generally only detectable when the temporal scale is sufficiently small since more global views show other dominating forces such as precipitation events (Nagorski et al. 2003). A number of studies have documented diel cycles. Bourg and Bertin (1996) found that pH, iron, temperature, and dissolved oxygen among others exhibited diel cycles in the Lot River in southwestern France. Iron fluctuations can be attributed in part to oxidation induced by light (Bourg and Bertin 1996). pH diel cycles have multiple causes including temperature change. However, the Lot River pH change of 0.4 pH units was attributed to photosynthesis and respiration of aquatic biota according to the Redfield equation:

$$106CO_2 + 16NO_3 + HPO_4^{2-} + 122H_20 + 18H^+ \leftrightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2 \qquad \text{Equation 2-4}$$

The forward reaction represents photosynthesis and the backward reaction represents respiration (Bourg and Bertin 1996). During the day photosynthesis consumes hydrogen ions and causes the pH to increase. At night photosynthesis ceases and respiration dominates causing hydrogen ions to be produced thus lowering the pH. According to Equation 2-3 nitrate should also exhibit a diel cycle but was not observed in the Lot River

(Bourg and Bertin 1996). A previous study in the GRSM only detected a diel cycle in water temperature (Silsbee and Larson 1982).

9. Variable Precipitation pH

Precipitation is a dominating factor in stream water quality. It is important to understand how precipitation varies in order to better understand how it affects stream water quality. Several studies will be reviewed to assess variable precipitation.

A meteorological study had 81 precipitation collectors that collected 941 samples (88 dry and 853 storm event) over a 444,788 acre study area in St. Louis, MO (Semonin 1976). The study found that the collected dry samples (analyzed with addition of laboratory reagent water) and storm events samples had variable pH. The dry samples had a fairly normal distribution with a pH mean of 7 (Semonin 1976). The storm samples exhibited a bimodal distribution of pH with 12.6% of the data equal to or less than 4 and 27.2% equal to or greater than 7 (Semonin 1976). This leaves 60.2% of the samples between pH 4 and 7. The meteorological study also found that the mean pH varied over the study area (Semonin 1976). The area mean precipitation pH was 4.9 (Semonin 1976). This is slightly higher than the mean precipitation pH in the GRSM collected in a similar manner (Robinson et al. 2003). However, it is important to note that the meteorological study collected its sample within 48 hours unlike for the GRSM data where precipitation samples are collected every two weeks.

Another study collected individual 25 ml samples over the course of single storm events to assess variability of pH during storm events in Tucson, Arizona (Seymour et al. 1976). pH varied from 4.51 to 6.08 for one storm event and 4.21 to 6.59 for a separate storm event. The Arizona study found that the maximum pH was seen at the onset of the

storm event similar to findings in this study. Interestingly, the Arizona study also found that acidic components varied over the length of collection period. Fluctuations of ammonia, carbonate, and bicarbonate were observed (Seymour et al. 1976).

Railsback (1997) found an association between lighting strikes and lower pH. Samples collected while thunder was heard had a mean pH of 3.63 which was less than mean of 4.05 of all combined samples. It was also found that samples collected during the day had a lower mean pH than samples collected at night. Wind coming from the direction of industrialized areas produced lower mean pH (Railsback 1997). Variation in pH during a single storm event may be partially explained by lower pH associated with lighting, time of rainfall, and direction of wind.

10. Statistical Approaches to Understanding and Describing Water Quality

Numerous theses and papers produced from data collected within the GRSM have used statistical approaches to understand and describe water quality. Harwell (2001) used time tread analysis to identify a decline in pH over time and used regression to identify geology as a major factor in predicting pH among others. Barnett (2003) used multiple linear regressions to describe and predict median pH, nitrate, sulfate, and ANC using elevation and other hydrologic variables. Multiple statistical techniques were used to model and identify trends in the Noland Divide Watershed, a high elevation watershed within the GRSM (Robinson et al. 2003). Descriptive statistics, multiple linear regression, time trend analysis were used to describe water quality. Nitrate and ANC was shown to be decreasing over time while chloride was shown to increase. pH, potassium, and sulfate did not exhibit time trends. Linear regression models developed had r^2 values ranging from 0.260 for chloride concentration model to 0.986 for sulfate load model

(Robinson et al. 2003). A number of studies have used statistical comparison techniques to assess any significant differences between water quality upstream and downstream of construction activities (Holt et al. 2003 and Hedrick 2002).

11. First Flush

The "first flush" is the initial run-off that occurs at the beginning of a storm event and is generally thought to contain a heavy pollutant load. The first flush contains pollutants that accumulate during antecedent periods which may be months or days. Defining the first flush can be difficult. There are several proposed definitions that include the amount of precipitation that has fallen or some amount of mass accumulated by the time some amount of volume has been received by the stream. This problem is confounded since pollutants peaks can vary during the same storm event (Lee et al. 2001). One definition states that 90% of pollutants are washed into the stream by the first 0.6 inches of rain (Farm 2002). This definition is not very practical since it is misleading to assume that every storm and every pollutant will have accumulated 90% of its mass in the first 0.6 inches of rain. Others have proposed that at least 80% of pollutant mass in the first 30% of storm run-off or 50% of the pollutant mass in the first 25% of the volume (Bertrand et al. 1998 and Wanielista and Yousef 1993).

Chapter III. Monitoring Methodology

1. Watershed Description

The Little Pigeon River (LPR) Watershed is defined as the area that drains to the portion of the Little Pigeon River located entirely within the boundary of the Great Smoky Mountain National Park (GRSM). The LPR watershed has an area of 30636.59 acres (47.87 square miles) and contains 107.95 miles of streams. Elevations within the watershed range from the highest point of 6621 feet to the watershed outlet elevation of 1370 feet. The dominant soil type in the watershed is Ramsey shaly silt loam. Other soil types found are Jefferson stony fine sandy loam, Sequatchie silt loam, Staser silt loam, Hamblen fine sandy loam, and stony colluvium. Anakeesta is found in the southern most parts of the watershed.

2. Monitoring Sites

There are a total of six monitoring sites within the LPR watershed: four stream and two precipitation monitoring sites (Figure 3-1). Sites 1 – 4 are stream sites and sites 5 – 7 are precipitation sites.

2.1 Stream Monitoring Sites

2.1.1 Stream Sites 1 – 3

Sites 1 – 3 are located on the Little Pigeon River and were designed to encompass the entire scheduled road construction. Site 1 is at the park boundary next to US HWY 321 approximately 1 mile north of the ranger station. Site 2 is approximately half a mile north of the Greenbrier ranger station and is located in the middle of the proposed construction.

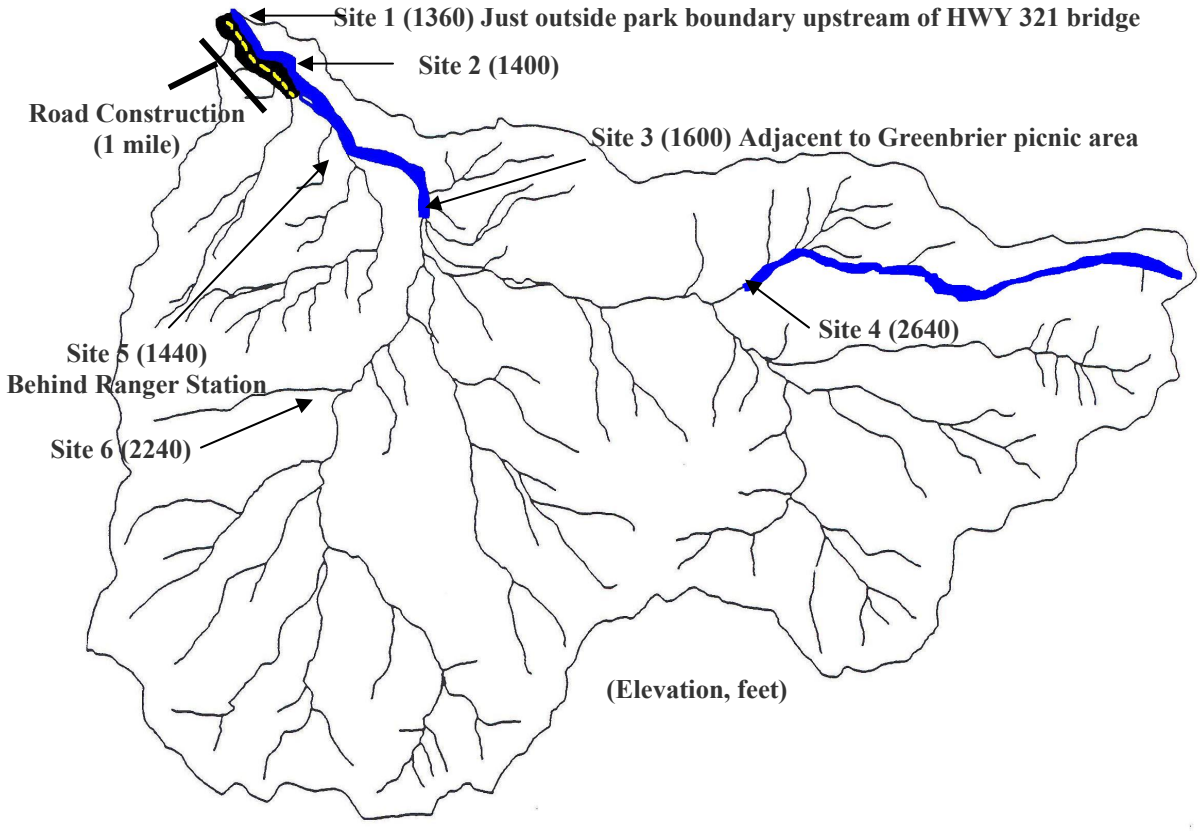

Figure 3-1. LPR watershed with monitoring sites.

Site 3 is approximately 2 miles south of the ranger station adjacent to the Greenbrier picnic area and is above proposed construction.

2.1.2 Stream Site 4

Site 4 is located on Ramsey Creek, which joins with Porters Creek to form the Little Pigeon River. Brook trout were historically found in this reach but are no longer present. It was thought that monitoring this reach could provide insight into why brook trout are no longer found. Even though this site was not placed as a result of scheduled road construction it still provides valuable information into the understanding of the watershed dynamics.

2.2 Continuous Stream Monitoring

2.2.1 YSI Sondes

Each stream site had a continuous monitoring YSI 6920 sonde (Figure 3-2). Sites 1 – 4 contained probes that recorded 15-minute pH, conductivity, temperature, and stage. Sites 1 – 3 also contained a probe that measured 15-minute turbidity. To further understand the diel (diurnal/nocturnal) cycle seen in the pH measurements, a dissolved oxygen probe was installed on the Site 1 sonde in late May 2004 of the preconstruction study.

2.2.2 Sonde Installation

Sites 1-4 each had a metal fence post driven into the streambed behind a medium sized rock (Figure 3-3). A four-inch diameter PVC pipe with multiple one-inch holes drilled into it was securely attached to the fence post. The sonde would then be placed inside the PVC pipe. The PVC pipe would then be capped. A hole in the cap allowed the

Figure 3-2. YSI 6920 sonde (courtesy of YSI www.ysi.com).

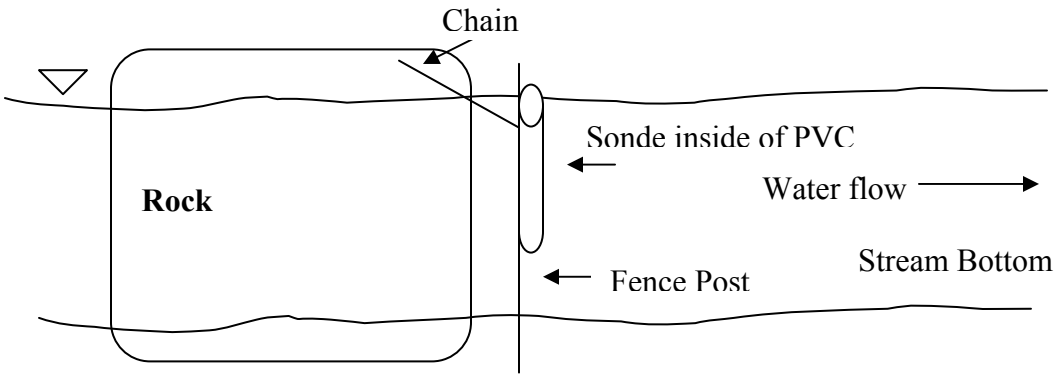

Figure 3-3. Sonde installation illustration.

sonde to be chained to the medium sized rock with a pad lock. The chain was anchored to the medium sized rock by drilling a hole and placing a concrete anchor in the hole. Nylon mesh with ¼ inch holes were later installed around the PVC pipes of sites 2 and 3 to allow water circulation but screen out gravel and other debris. This method met all predetermined parameters for safety, security, and quality measurements, specifically:

1. Good flow to the sensors
2. Protection from debris
3. Anchorage to withstand high flow
4. Security from theft or vandalism
5. Accessible to project personnel
6. Not pose a danger to park visitors

2.2.3 Sonde Maintenance and Calibration

During most visits to the watershed, the sondes were inspected for damage and lodged debris. To ensure accurate measurements, each sonde was calibrated for all measured parameters every one to two months. Calibration and maintenance was performed according the manufacturers recommendations.

2.3 Baseline Grab Samples

To establish baseline conditions bi-weekly grab samples were taken at Sites 1 – 3. Site 4 grab samples were collected every two months. Grab sample were collected in 250 ml plastic bottles by first rinsing the bottle three times with stream water then submerging and capping the full bottle under water. Samples were collected 5 – 15 feet from the stream bank by using either an adapted sampling pole or entering the stream using chest-waders.

2.4 Storm Event Samples

In addition to the use of continuous monitoring sondes, on a storm event basis water samples were collected using automatic samplers at Sites 1-3. Stage measurements from the sondes were sent to Campbell Scientific CR-10 data-loggers. The data-logger then compared the reading to a preset stage value. If the value was exceeded it would then send a signal to an Isco brand auto-sampler. At the initiation of the sampling cycle, the auto-sampler first flushed the intake line with stream water then took a sample. The data-logger was programmed to have the auto-samplers take four samples at fifteen minute intervals followed by twenty samples at one hour intervals. Select samples were then chosen to provide an overview of storm water quality. Storm samples collected provided a very good snapshot of the water quality seen during a storm event as Figure 3-4 illustrates. The auto-samplers were powered by marine batteries and the data-loggers were powered by small seven amp-hr batteries. Each was recharged by voltage regulated solar panels.

2.5 Precipitation Sites

To better understand the effects precipitation has on the water quality within the watershed, two precipitation stations were installed in the watershed. The traditional definition of an open site is defined by a 45^{o} clearance on all sides of the site. No site found strictly meets this definition nor could be created in the protected park. The most appropriate sites were selected that were easily accessible to project personnel. The open sites each had a tipping bucket rain gauge that measured in 0.01 inch increments and an ordinary field rain gauge to ensure the accuracy of the tipping buckets. It was found that the tipping buckets measured the total volume within 0.05 inches of the field rain gauge.

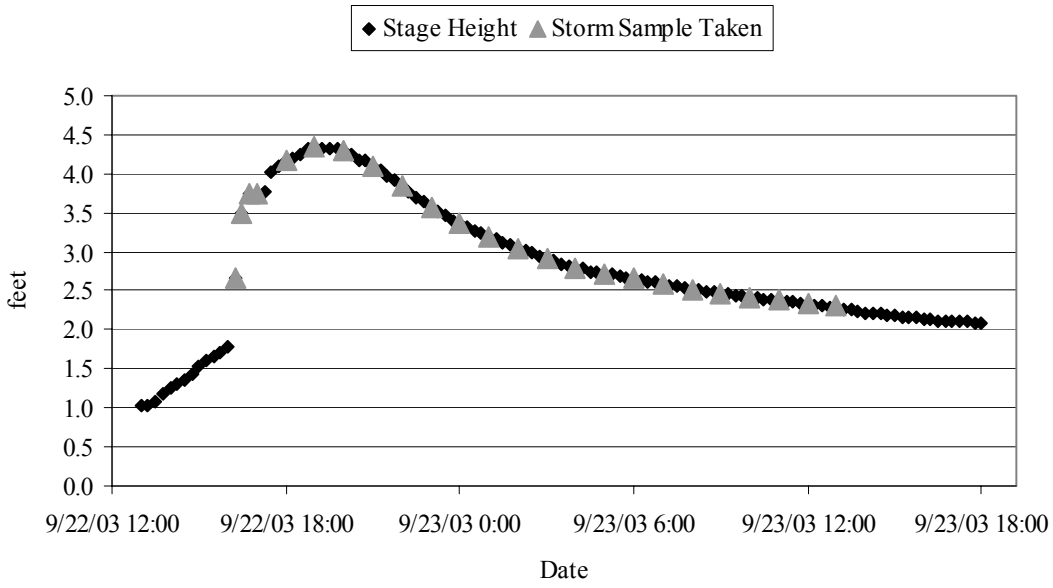

Figure 3-4. Example storm sample collection by auto-samplers at Site 2.

Initially sites 5 – 6 each had a single bulk collector to measure combined wet and dry atmospheric deposition. The measured parameters for the two samples locations were found to be very similar and one collection point was deemed sufficient. One sequential precipitation collector was rotated between the two precipitation sites. The collector was based on the design described by Vermette and Drake (1987). An eight-inch diameter funnel collected and directed precipitation into 50 mL sample bottles. Once the first bottle is filled, the water is diverted to the next bottle. The collector differed from the design basis in that it collected wet and dry deposition. Depending on the size of the storm event, up to four bottles were filled and collected.

2.6 Chemistry Analyses

All samples were analyzed for pH, conductivity, and ANC using a Mantech auto-titrator. Sodium, potassium, magnesium, calcium, manganese, iron, silicon, copper, zinc,

and aluminum were run using an inductively coupled plasma (ICP) unit. Chloride, nitrate, and sulfate were analyzed using an ion chromatographic method (IC).

2.7 Quality Assurance and Quality Control (QA/QC)

All test procedures used to chemically analyze water samples were based upon published methods (Table 3-1). These procedures were used to analyze all samples as discussed in the Chemical Analyses section. All samples were analyzed at room temperature. Each test procedure had internal QA/QC in the form of spikes, splits, and replicates. There will be a formal QA/QC report prepared for the National Park Service documenting the results at a later date.

In addition to internal QA/QC samples, 15% of base flow grab samples collected were QA/QC samples which included splits and replicates. Approximately 5% of storm samples collected were QA/QC samples which only included splits. QA/QC samples received lab codes and were undistinguishable from ordinary samples. The average percent difference for all sample splits and replicates are shown in Table 3-2. Acceptable reproducibility for all parameters was found except for iron and manganese. This was expected since these constituents are found in low concentrations in park waters. Ion balances were also used to for all samples to judge quality of results as calculated by the U.S. EPA (Hillman el al. 1986.) Average ion balances for all samples are shown in Table 3-3 by site. Table 3-3 show that the average absolute value of the ion balances was 8-9% which falls within EPA's guideline of less than 15%. The ion balances were negative which indicates some anions are present that were not measured. Possible anions present but not measured are organic and silicate acids.

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

Analysis	Procedure	Equipment	Method Reference
pH	Potentiometric	PC-Titration Plus	EPA Method 150.1
Conductance	Potentiometric	PC-Titration Plus	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus	Automated Gran Titration for low ionic strength waters as in Hillman et al. 1986
Anions (NO_3^-, Cl^-, SO_4^{2-})	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Metals	Inductively Coupled Plasma	Thermo-Elemental IRIS Intrepid II ICP	EPA Method 6010B and 6010C

Table 3-2. Average percent difference for sample splits and replicates for base and storm flow QA/QC samples. (n=24).

Parameter	Average Percent Difference
Conductivity	4.21%
pH	0.49%
ANC	-8.85%
Chloride	-2.04%
Nitrate	13.90%
Sulfate	-12.62%
Al	-5.58%
Ca	0.80%
Cu	19.91%
Fe	-51.62%
K	-18.60%
Mg	1.72%
Mn	31.33%
Na	-1.01%
Si	1.64%
Zn	-15.69%

Table 3-3. Average ion balance for all samples by site.

	Average Ion Balance
Site 1	-8.32%
Site 2	-8.55%
Site 3	-8.97%

Laboratory reagent water blanks were taken to the field every time base flow QA/QC samples were collected and ideally have close to zero concentration of the ions measured except hydrogen. pH of laboratory water was always 5.0 +/- 0.25 pH units. The mean conductivity for laboratory reagent water blanks was 0.98 μS/cm. Higher-grade laboratory reagent water was used in the latter part of this study with improved results.

3. Data Collection in Natural Environments

Working in natural environments can prove to be challenging in that people and equipment are not always able to deal with harsh environments. Water temperature ranged from zero to twenty degrees Celsius based on sonde data and air temperature ranged from zero to thirty degrees Celsius based on monthly averages published by the National Park Service for Gatlinburg, TN. In addition to a wide range of temperatures, the area receives a significant amount of annual rainfall. High intensity precipitation events result in stream flows that carry great energy and force. These combined effects sometimes resulted in some lost data and damaged equipment.

3.1 YSI Sonde Problems

The sonde deployment method was good, but even so problems were encountered. During a major storm event on November 18, 2003, the glass bulb on the Site 3 pH sonde probe was ruptured from small pebbles being wedged in the guard and probes. A new pH probe was ordered and installed on December 9, 2003. Following this event a nylon mesh was installed at Site 2 and 3 with no further significant damage. During several storm events the wipers on the turbidity probes from each site were torn off. Once the stream stage allowed, the wipers were replaced. During a storm event beginning September 8, 2004, high water velocity ripped the PVC pipe containing the sonde at Site

3 from the supporting fence post. Fortunately, the sonde was also securely fastened to a nearby rock by a metal chain and no damage occurred. A storm event occurring sometime after September 8, 2004 pulled the sonde from Site 4 out of the PVC pipe and wedged it between two rocks. The sonde would not respond and required repair from the manufacturer for further use. Even minor maintenance proved to be difficult when frequent storm events prevented stream stage from subsiding enough to allow access to sondes.

3.2 Isco Auto-sampler and Campbell Data-logger Problems

A storm event on November 18, 2003 resulted in high water levels at each of the sites. The auto-sampler located at Site 2 was pushed on its side and its lid washed downstream. This same storm event moved the battery and auto-sampler at Site 3 downstream until the cables they were attached to halted their movement. A storm event on September 8, 2004 also broke a stress relief cable at Site 3 resulting in the intake tubing and sonde cables to be torn lose from the auto-sampler and data-logger. The tubing and cable were also attached to the PVC pipe and were recovered.

A common problem was battery failure. Battery failure of the auto-samplers resulted in storm samples not taken. Power failure for the data-loggers resulted in lost data. To help offset this problem an extra solar panel was installed at each site to allow one solar panel per battery. Additionally, the sondes were set to independently log at a thirty-minute interval to ensure minimum data loss in the event the data-logger stopped recording.

3.3 Hobo Data-logger Problems

The Hobo data-loggers used to log precipitation data are of simple design by comparison to the Campbell Scientific data-loggers used at the stream sites. The Hobos contain a small circuit board encased in a similarly small plastic case that records the time and date the tipping bucket rain gauge receives 0.01 inch of rain. The 0.01 inch of rain is recorded when a magnet on the bucket activates an electric pulse via a reed switch as the tipping bucket tips. Persistent problems were encountered with the Hobos. Several times the Hobos failed to record data and had to be sent back to the manufacturer. Each time the problem was attributed to water corrosion. The Hobos are designed to be weather resistant but did not meet the challenges put forth by the LPR watershed.

IV. Data Summary and Overview

1. Introduction

This chapter presents an overview of the water quality collected from the stream and precipitation sites in the Little Pigeon River (LPR) watershed. These data are also analyzed by a variety of statistical and graphical techniques.

2. Sonde Data for Sites 1 – 4

This section presents descriptive statistics and graphs of the sonde data. All statistics in this chapter and future chapters were calculated using JMP 5.1.1.

2.1 Sonde pH

Sonde stage and pH vs. time for Site 2 and 4 are shown in Figure 4-1 and 4-2. Both sites illustrate the responsiveness of pH to increased stage. Downward pH dips are nearly mirror images of stage and clearly show the drop in pH during storm events. Additionally, upward pH spikes are apparent and occur at the onset of a storm event. This will be discussed in more detail in Chapter 7. Figure 4-1 and 4-2 also illustrates that Site 2 and 4 approached pH 5 several times. Site 4 dipped below pH 5 a number of times and dipped below pH 4 one time. Waters with pH less than 5.5 are considered acidic (Lachance and Bobee 1991). Using this criterion all sites had periods of acidic water.

Each sonde pH reading approximately represents the water quality for a fifteen or thirty minute period depending on the logging interval of the sonde. Thus the total time represented by the data for Site 2 is 339.09 days. Figure 4-3 shows that only 0.36% of the data are below the acidic level of 5.5. The total time that the pH dipped below 5.5 corresponds to 1.21 days. Sites 1 and 3 had similar results. This indicates that overall the

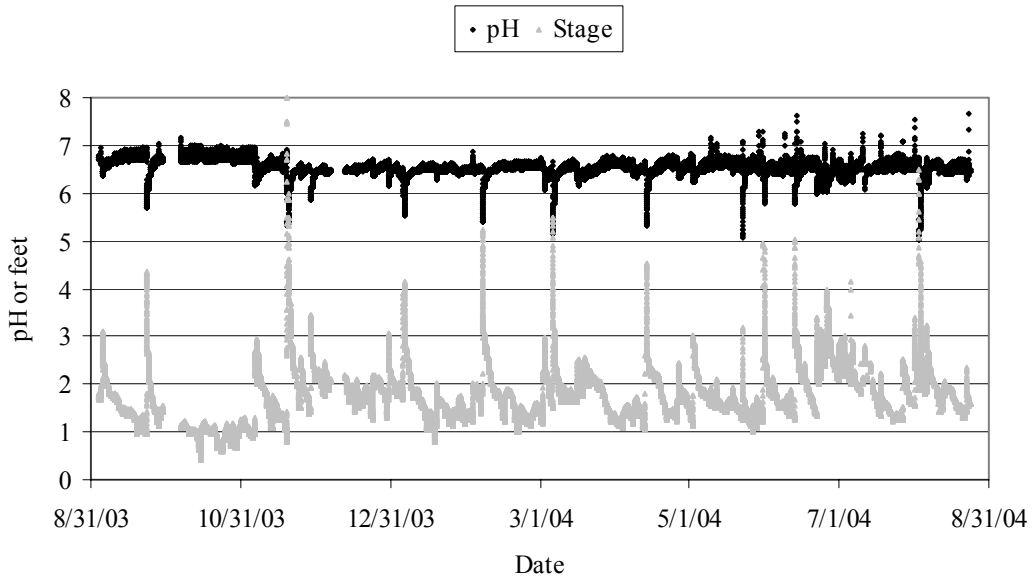

Figure 4-1. Sonde stage and pH vs. time at Site 2 (n = 32,000).

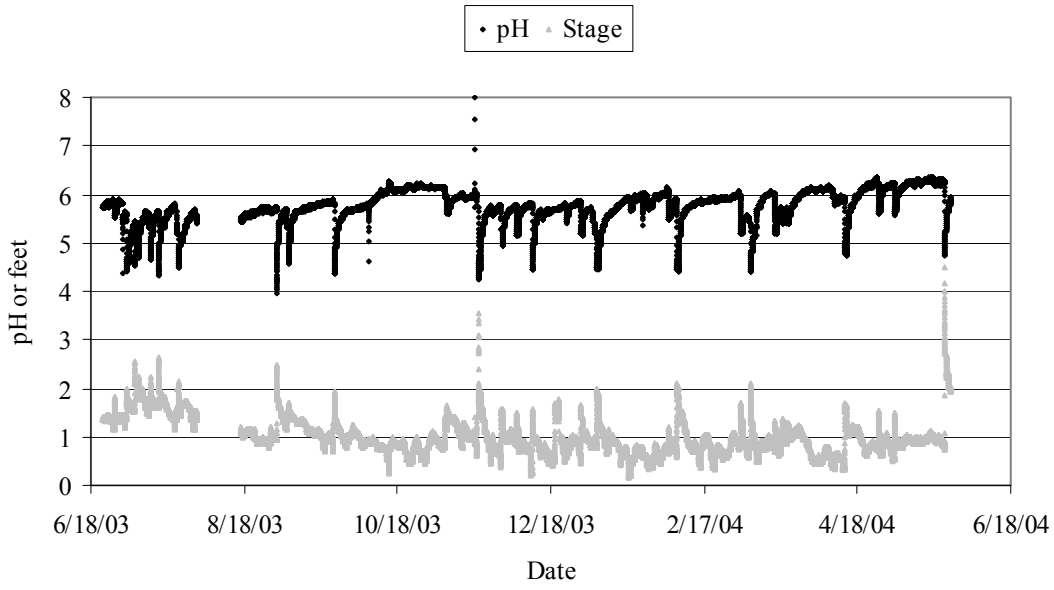

Figure 4-2. Sonde stage and pH vs. time at Site 4 (n = 30,761).

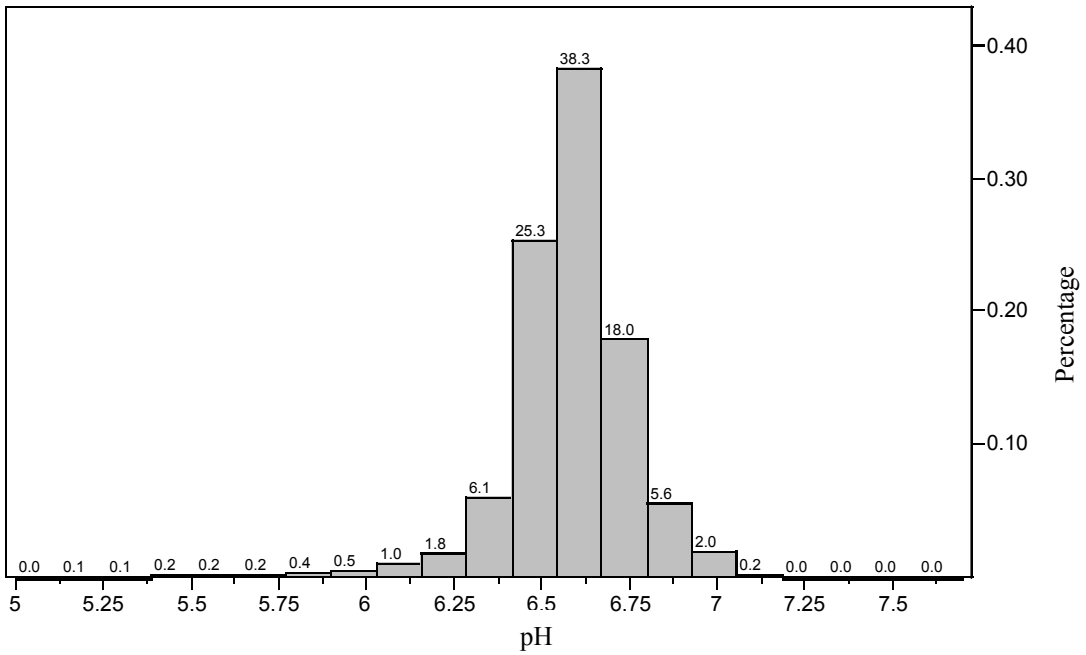

Figure 4-3. Histogram of sonde pH at Site 2 (n = 32,243).

water quality at Sites 1 – 3 is healthy in terms of pH. Site 4 had different results. Figure 4-4 represents 320.42 days for Site 4. Site 4 was below pH 5.5 for forty-five days (14.3 % of the time) which is arguably chronic acidification and unsuitable for aquatic life. This does not however represent the connected duration that the pH was under 5.5. There are a number of documented occasions of episodic acidification but Sites 1 -3 are not plagued by chronic acidification. Site 4 however spends considerable time in the 4 – 5.5 range. This combined with a mean $[H^+]$ of 5.57, indicates chronic acidification at Site 4.

Sonde pH descriptive statistics are shown in Table 4-1. A number of observations were made based on Table 4-1.

- Sites 1, 3, and 4 reached or exceeded stream pH of 8.0. Site 2 had a maximum pH of 7.65. The maximums were 1.12 to 2.32 pH units above mean stream pH.
- Minimum pH values ranged from 3.96 at Site 4 to 5.04 at Site 2.
- The pH range for each site varied from 2.06 to 4.04 but the significantly lower inter quartile range (IQR) indicates that the majority of the data are in a much narrower range. The IQR is the width of an interval which contains the middle 50% of the data. This is due to the large quantity of base flow data collected.
- The mean pH at all four stream sites were above pH 5.5 although Site 4 mean pH did approach 5.5 with a mean pH of 5.76.
- There has been some debate on the appropriateness of taking the mean of $[H^+]$ directly. Sonde pH values were converted to hydrogen concentration then the mean taken. A 0.05 to 0.18 lower mean pH was obtained after the $[H^+]$ mean was transformed to pH. This brought mean stream pH at Site 4 much closer to the pH 5.5 acidic criteria.

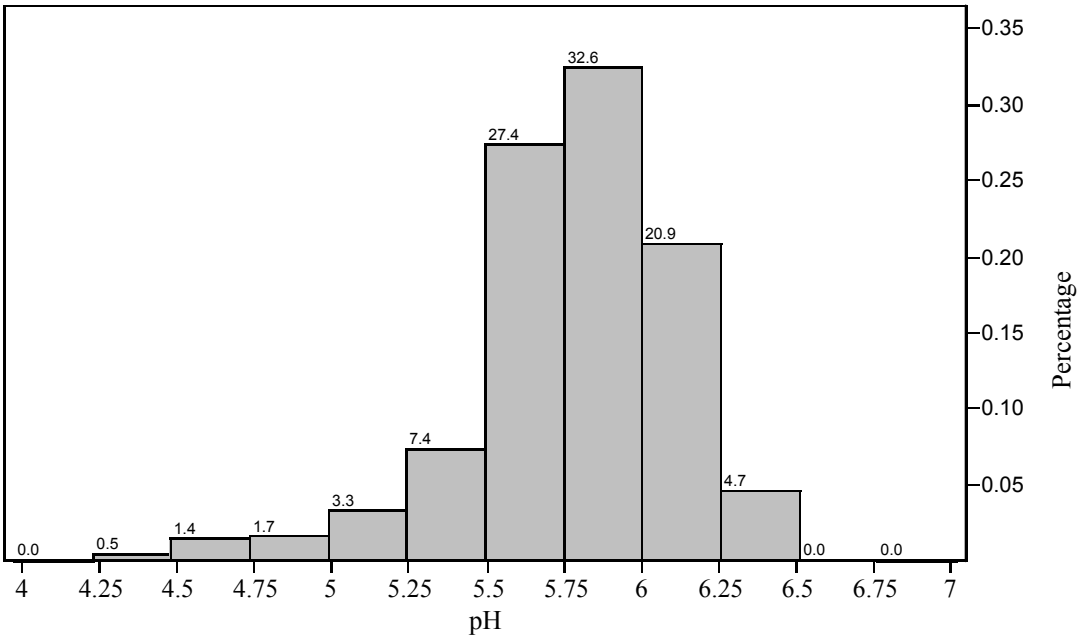

Figure 4-4. Histogram of sonde pH at Site 4 (n = 30,760).

Table 4-1. Sonde pH descriptive statistics for Sites 1 – 4.

	Stream Sites			
	Site 1	**Site 2**	**Site 3**	**Site 4**
Elevation, ft	1370	1400	1600	2560
Dates	8/25/03 - 9/15/04	9/3/03 - 8/28/04	8/20/03 - 9/15/04	6/23/03 - 5/25/04
		pH statistics		
Maximum	8.77	7.65	8.38	8.00
Q_3	6.58	6.63	6.46	5.98
Median	6.45	6.53	6.38	5.79
Q_1	6.34	6.46	6.27	5.61
Minimum	4.98	5.04	4.77	3.96
Range	3.79	2.61	3.61	4.04
IQR	0.24	0.17	0.19	0.37
Mean	6.45	6.53	6.34	5.76
Std Dev	0.23	0.18	0.20	0.34
Skewness	-0.73	-1.63	-1.91	-1.15
Kurtosis	5.31	9.22	9.61	2.30
$[H^+]$ Mean	6.37	6.48	6.27	5.57
N	30720	32243	25076	30760

Based on the histograms in Figures 4-3 and 4-4, sonde pH at Sites 2 and 4 visually appear to have a fairly normal distribution. However, pH values seen during storm events resulted in a number of outlying points. This skews the histogram distribution toward lower pH. This is confirmed by the skewness seen in Table 4-1. Data with exact symmetry will have zero skewness. All four stream sites were negatively skewed. A goodness of fit test could be employed to test for normality although large data sets often reject normality at any reasonable confidence level. A normal quantile plot provides a visual measurement of normality. Normal quantile plots are shown in Figure 4-5 and 4-6 for Sites 2 and 4, respectively. Extreme departure from the plotted straight line indicates lack of normality.

2.2 Sonde Turbidity

Figure 4-7 illustrates turbidity responsiveness to stage. Increased stage generally caused turbidity to increase. The Minnesota Pollution Control Agency has proposed streams be deemed impaired once turbidity has reached 25 NTU although no duration was given (Vondeacek et al. 2003). Turbidity often approaches and exceeds 25 NTU. Turbidity also exceeded 100 NTU on a number of occasions and approached 1000 NTU at Sites 1 – 3.

The median turbidity was for Sites 1 – 3 was well below the proposed 25 NTU standard (Table 4-2). The mean turbidity was higher compared to the median but was still below the 25 NTU standard. Over seventy-five percent (Q_3) of the turbidity data for all sites was under 25 NTU indicating acceptable turbidity levels.

Visual inspection of Figure 4-8 shows that turbidity had a positive skewed distribution. This is confirmed by the positive skewness values given in Table 4-2. The

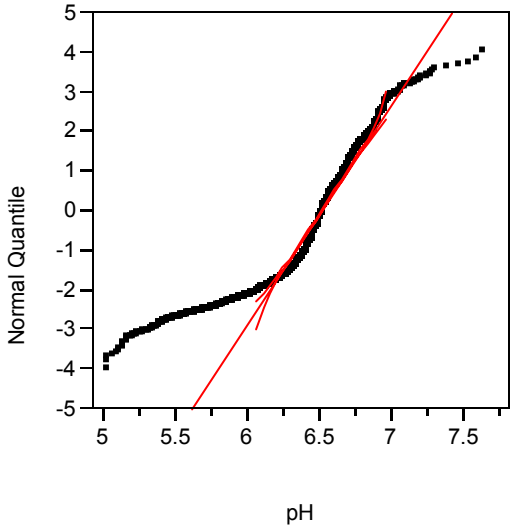

Figure 4-5. Normal quantile plot of Site 2 sonde pH.

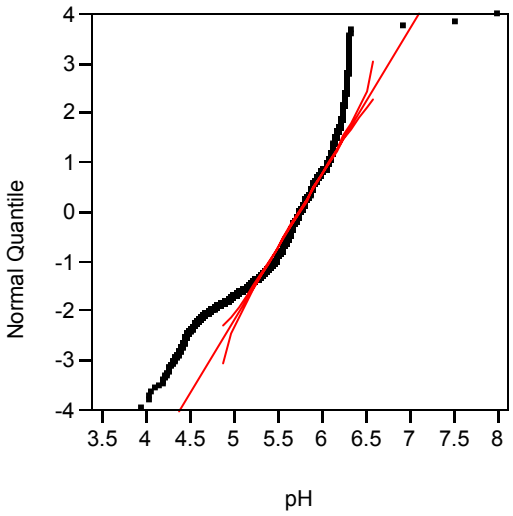

Figure 4-6. Normal quantile plot of Site 4 sonde pH.

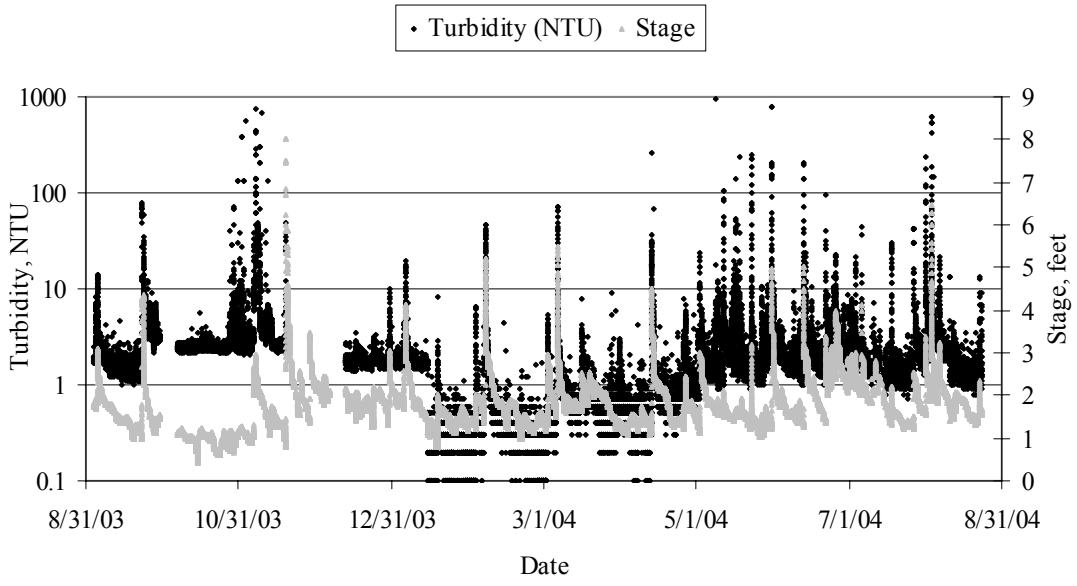

Figure 4-7. Sonde stage and turbidity vs. time at Site 2 (n = 32,000).

Table 4-2. Sonde turbidity descriptive statistics for Sites 1 – 3.

	Stream Sites		
	Site 1	**Site 2**	**Site 3**
	Turbidity (NTU) statistics		
Maximum	1286.90	1264.40	1382.40
Q_3	4.80	2.40	9.60
Median	3.30	1.70	5.60
Q_1	1.50	0.80	1.00
Minimum	0.30	0.00	0.00
Range	1286.60	1264.40	1382.40
IQR	3.30	1.60	8.60
Mean	6.38	3.57	12.76
Std Dev	34.26	31.34	70.72
Skewness	29.09	31.98	14.54
Kurtosis	964.82	1136.36	229.93
N	30277	30553	24987

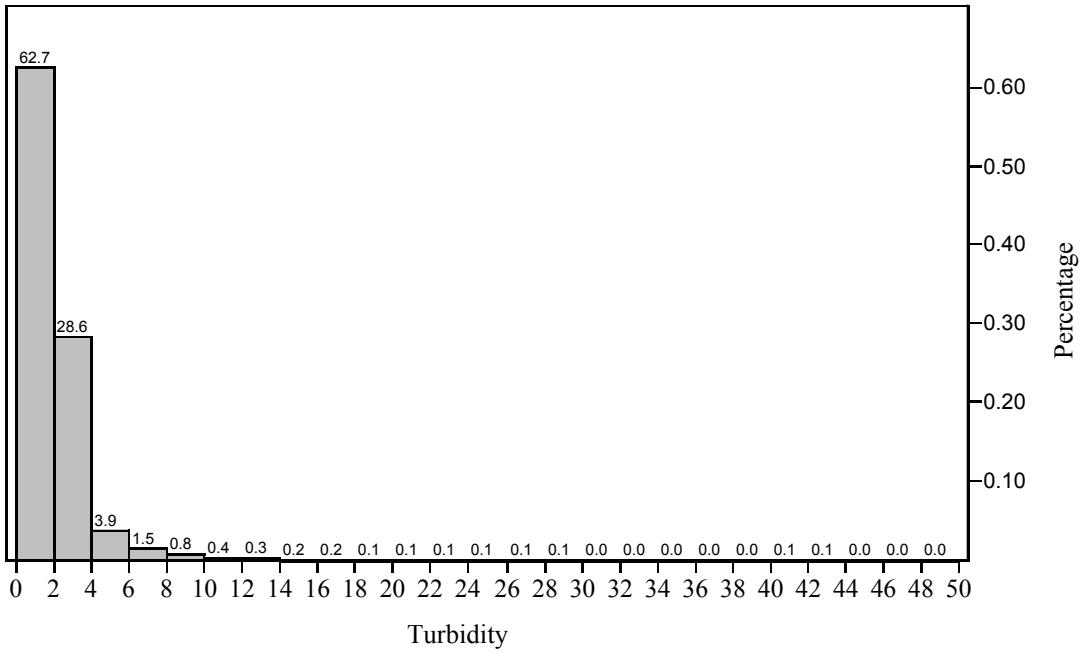

Figure 4-8. Histogram of sonde turbidity (NTU) at Site 2 (n = 30553).

normal quantile plot in Figure 4-9 clearly shows extreme departure from a normal distribution.

A similar approach used in finding pH under 5.5 finds that the total time represented by turbidity data are 321.50 days for Site 2. Only 1.12% (3.60 days) of the time was turbidity above 25 NTU at Site 2. Sites 1 and 3 had similar results.

2.3 Sonde Temperature

Various temperature criteria for brook and rainbow trout are given in Table 4-3. The mean temperature for Sites 1 – 3 was close to twelve and about nine degrees Celsius for Site 4 (Table 4-4). This is below the maximum average weekly temperature for juvenile growth for both species. At least 75% of the data (Q_3) was also below this maximum. Sonde water temperature illustrated an interesting bimodal distribution. This is likely representative of cold periods during winter months followed by a transition temperature period to warmer summer months and vice versa in addition to daily variation (Figure 4-10).

3. Base flow Grab Sample Data for Sites 1 – 4

This section will cover descriptive statistics and graphs for stream grab samples collected at Sites 1 – 4. All samples were collected during base flow.

3.1 pH

A pH standard given in Table 2-1 classifies stream pH in the range of 6 to 7 as unlikely to be harmful to fish. The base flow pH of Sites 1 and 2 were in this range. All baseline grab samples at Site 2 were in the 6 – 7 pH range (Figure 4-11). Site 3 baseline pH exceeded the lower boundary thirteen times but is still unlikely to be harmful to fish (Figure 4-12). Additionally, the median or mean pH does not indicate problems with

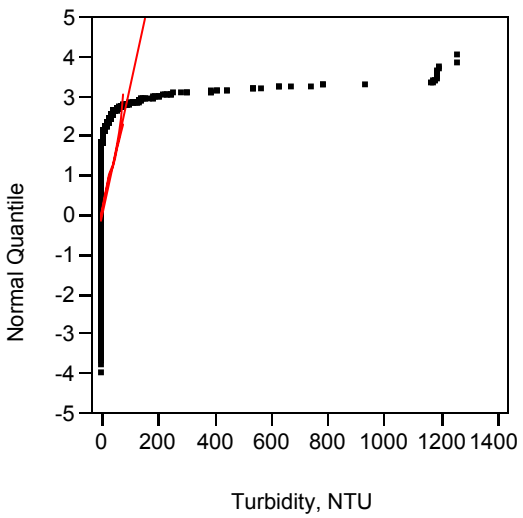

Figure 4-9. Normal quantile plot of Site 2 sonde turbidity.

Table 4-3. Maximum average temperatures for growth and short-term maximum temperatures for selected fish (Brungs and Jones 1977).

Species	Max. Weekly average temp. for growth (juveniles)	Max. Temp. for survival of short exposure (juveniles)	Max. Weekly average temp. for spawning [a]	Max. Temp. for embryo spawning [b]
Brook trout	19 °C (66 °F)	24 °C (75 °F)	9 °C (48 °F)	13 °C (55 °F)
Rainbow trout	19 °C (66 °F)	24 °C (75 °F)	9 °C (48 °F)	13 °C (55 °F)

a - Optimum or mean of the range of spawning temperatures reported for the species

b - Upper temperature for successful incubation and hatching reported for the species

Table 4-4. Sonde descriptive statistics for conductivity and temperature.

	Stream Sites			
	Site 1	**Site 2**	**Site 3**	**Site 4**
	Conductivity (µS/cm) statistics			
Maximum	35.00	33.00	30.00	26.00
Q_3	17.00	16.00	15.00	12.89
Median	16.00	16.00	14.00	12.00
Q_1	16.00	15.00	13.00	5.00
Minimum	12.00	7.00	2.00	0.00
Range	23.00	26.00	28.00	26.00
IQR	1.00	1.00	2.00	7.89
Mean	16.45	14.77	13.05	9.56
Std Dev	1.39	2.93	3.36	4.32
N	30720	32243	27053	30758
	Temperature (^{o}C) statistics			
Maximum	22.51	20.24	19.77	17.92
Q_3	16.57	15.72	16.12	13.86
Median	13.48	11.92	13.69	9.46
Q_1	7.33	6.40	7.31	4.46
Minimum	0.70	0.89	1.00	-0.55
Range	21.81	19.35	18.77	18.47
IQR	9.24	9.32	8.81	9.40
Mean	12.12	11.15	11.92	9.18
Std Dev	5.09	4.95	4.89	4.84
N	30720	32243	27053	30760

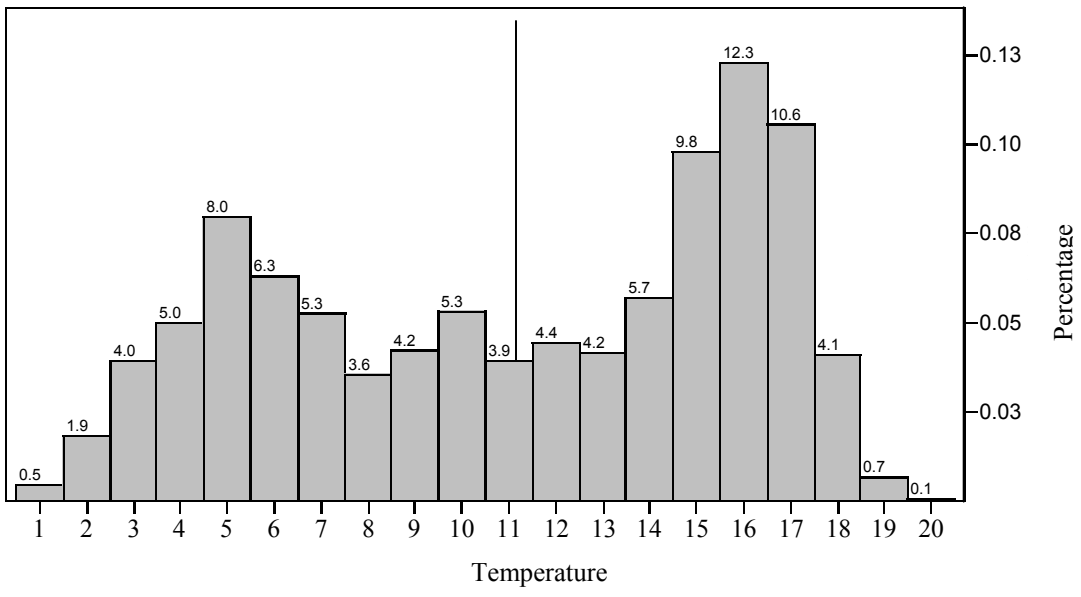

Figure 4-10. Histogram of sonde temperature (^{o}C) at Site 2 with mean temperature displayed as vertical line (n = 32243).

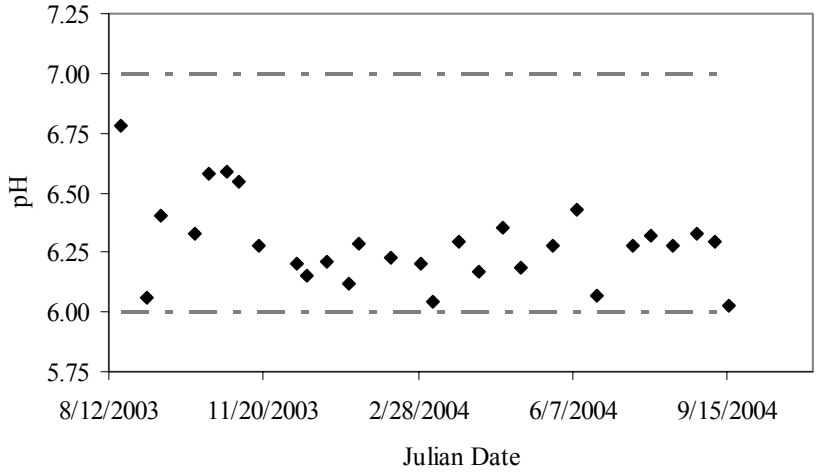

Figure 4-11. Baseline pH vs. time at Site 2 with pH 6 – 7 boundary markers.

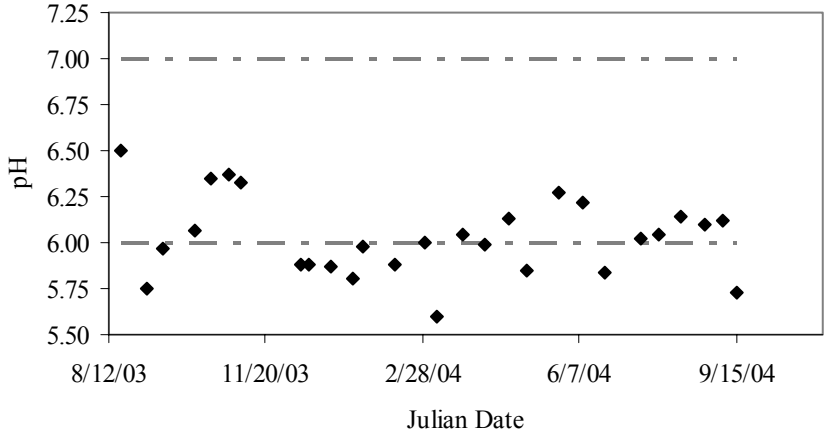

Figure 4-12. Baseline pH vs. time at Site 3 with pH 6 – 7 boundary markers.

chronic acidification at Sites 1 – 3. Overall baseline pH is acceptable at Sites 1 – 3. Site 4 stream pH was lower with mean and median 5.46 and 5.52. This indicates acidic stream water at Site 4.

In 2002, several stream sites in the LPR watershed were part of the GRSM stream survey in which base flow grab samples were collected every three months (Robinson et al. 2003). Stream survey site 52 samples were collected at the same location as Site 1 stream samples. The median pH for Site 52 stream samples was 6.16 (Robinson et al. 2003). This is close to the median stream pH at Site 1 of 6.24 (Table 4-5). There were no stream survey sites near Site 2. Stream survey site 49 was about 2000 feet upstream at an elevation about 70 feet higher than Site 3. Site 49 has a median pH of 6.14 which was higher than the median stream pH at Site 3 of 6.01 (Robinson et al. 2003). Stream survey sites 46 and 47 were located on the southwest side of the LPR watershed at elevations of 2750 and 2400 feet, respectively. Site 4 was at a similar elevation of 2560 feet but was on the southeast side of the watershed. Stream survey site 46 and 47 had median stream pH of 5.45 and 6.01, respectively. Site 4 had median stream pH of 5.52.

The median and mean for the base flow grab samples at Sites 1 – 4 are lower than values given in Table 4-1 for sonde pH data. This may simply represent slight changes in chemistry from the field to the laboratory due to equilibration with atmospheric CO_2. since the in-situ stream water may not be in equilibrium with CO_2 due to biological action, e.g., algal mass growing on rocks.

3.2 Acid Neutralizing Capacity

Streams with ANC (acid neutralizing capacity) below 200 μeq/l are considered to be sensitive to acidification (Lachance and Bobee 1991). The maximum ANC seen at any

Table 4-5. Stream base flow descriptive statistics for pH.

	Stream Sites			
	Site 1	**Site 2**	**Site 3**	**Site 4**
Dates	8/20/03 - 9/15/04	8/20/03 - 9/15/04	8/20/03 - 9/15/04	10/6/03 - 5/25/04
		pH		
Maximum	6.82	6.78	6.50	5.75
Q_3	6.35	6.34	6.14	5.74
Median	6.24	6.28	6.01	5.52
Q_1	6.12	6.18	5.87	5.11
Minimum	5.96	6.03	5.60	5.04
Range	0.86	0.75	0.90	0.71
IQR	0.22	0.17	0.27	0.63
Mean	6.25	6.29	6.03	5.46
Std Dev	0.20	0.17	0.21	0.34
N	29	29	28	4

of the stream sites was 103.62 μeq/l during base flow (Table 4-6). The median ANC was below 60 μeq/l for all stream sites. This is below 200 μeq/l indicating that all four sites are sensitive to episodic acidification. A newer study states that 50 μeq/l is a general guideline for acidification sensitivity (Sullivan et al. 2004). This indicates that only Sites 3 and 4 are acid sensitive. A general guideline for brook trout was also given for stream ANC as shown in Table 4-7 (Sullivan et al. 2004). Site 2 is generally in the 50 to 150 ANC range (Figure 4-13). Site 3 is generally in the 20 – 50 ANC range but drops to the 0 to 20 range several times (Figure 4-14).

Stream survey samples were also measured for ANC. Site 1 had a median stream ANC of 50.85 μeq/l which was somewhat higher than stream survey site 52 median ANC of 34.15 μeq/l. Stream survey site 49 had a median stream ANC of 19.63 μeq/l. This was lower than the median stream ANC of 29.07 μeq/l at Site 3. Stream survey sites 46 and 47 had median ANC values of 0.04 and 12.98 μeq/l, respectively. Site 4 median stream ANC was 11.60 μeq/l.

Table 4-6. Stream base flow descriptive statistics for anions.

	Stream Sites			
	Site 1	**Site 2**	**Site 3**	**Site 4**
			ANC (µeq/l)	
Maximum	96.20	103.62	68.65	17.52
Q_3	65.58	73.98	42.11	17.12
Median	50.85	58.52	29.07	11.60
Q_1	38.47	46.13	22.28	1.82
Minimum	25.74	36.40	12.80	0.00
Range	70.46	67.22	55.85	17.52
IQR	27.11	27.85	19.83	15.29
Mean	53.42	61.53	32.99	10.18
Std Dev	17.42	18.03	14.39	8.14
N	29	29	28	4
			Chloride (µeq/l)	
Maximum	19.47	19.98	18.95	14.74
Q_3	14.88	14.52	13.47	14.69
Median	12.19	12.08	12.13	13.46
Q_1	6.37	8.10	8.18	6.21
Minimum	3.66	3.30	3.35	4.15
Range	15.81	16.68	15.59	10.59
IQR	8.51	6.42	5.29	8.49
Mean	11.00	11.09	11.40	11.45
Std Dev	4.90	4.71	4.57	4.98
N	29	29	27	4
			Nitrate (µeq/l)	
Maximum	30.71	46.98	40.96	38.62
Q_3	22.35	27.00	26.91	37.37
Median	19.08	19.29	23.17	31.07
Q_1	12.80	11.95	16.59	20.27
Minimum	0.00	0.00	0.00	17.52
Range	30.71	46.98	40.96	21.10
IQR	9.55	15.05	10.32	17.10
Mean	17.83	19.87	21.73	29.57
Std Dev	7.77	11.16	8.64	9.03
N	27	29	24	4
			Sulfate (µeq/l)	
Maximum	49.13	62.21	66.42	37.04
Q_3	40.11	40.38	42.88	36.52
Median	37.21	38.07	38.86	32.26
Q_1	35.37	34.80	37.21	28.97
Minimum	27.45	26.12	29.42	28.78
Range	21.68	36.09	37.00	8.26
IQR	4.74	5.58	5.68	7.55
Mean	37.53	39.18	40.16	32.58
Std Dev	5.01	9.12	7.30	4.05
N	26	29	24	4

Table 4-7. ANC ranges for brook trout and acid sensitivity. (Sullivan et al. 2004).

ANC Range (μeq/l)	Suitability to brook trout	Acid Sensitivity
ANC ≤ 0	Unsuitable	Acidic
0 > ANC < 20	Marginal	Highly sensitive to chronic and acute acidification
20 > ANC ≤ 50	Indeterminate	Potentially sensitive to chronic and acute acidification
50 > ANC ≤ 150	Suitable	May be sensitive to chronic and acute acidification under possible future deposition

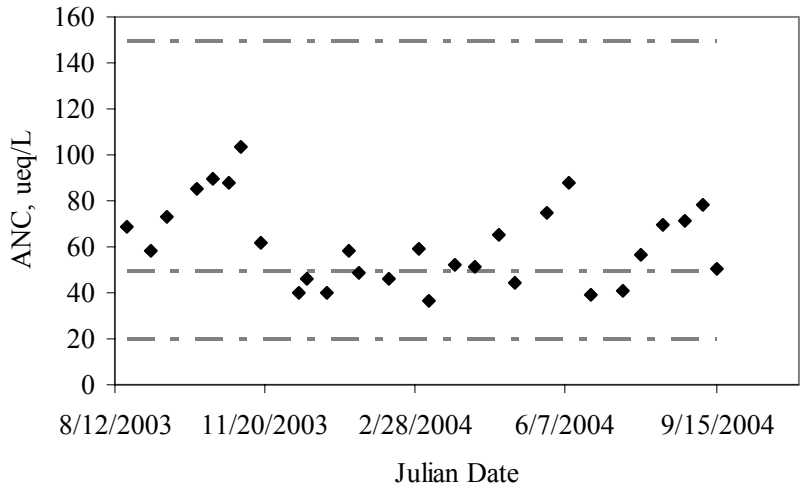

Figure 4-13. Baseline ANC vs. time at Site 2 with ANC 20 – 50 and 50 – 150 boundary markers.

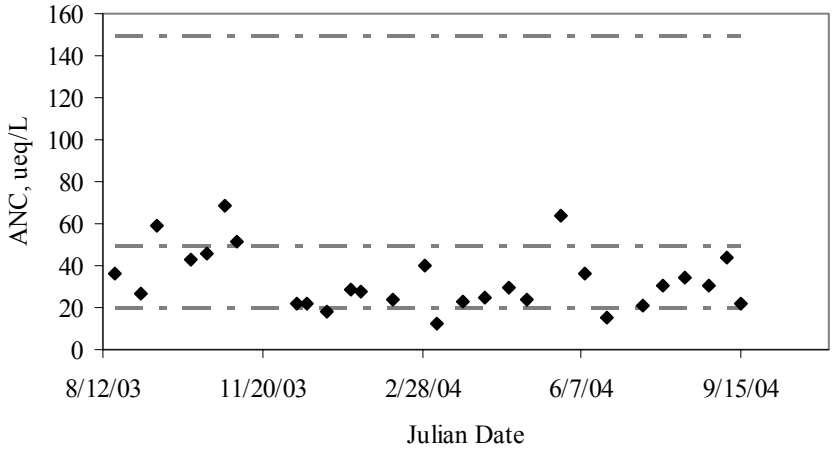

Figure 4-14. Baseline ANC vs. time at Site 2 with ANC 20 – 50 and 50 – 150 boundary markers.

The implications drawn from the above analysis are:

- The LPR watershed has little ability to neutralize acidic storm events.
- Large pH drops were observed since the buffering capacity of the watershed is easily overpowered.

3.3 Nitrate, Sulfate, and Chloride

Nitrate, sulfate, and chloride descriptive statistics of base flow samples are shown in Table 4-6. Nitrate follows the previously identified trend of increasing concentration with increasing elevation (Barnett 2003). Chloride and sulfate do not follow this trend but rather seem to be constant regardless of elevation. Also, elevated sulfate and decreased ANC concentrations are indicators of acid deposition. This indicates Site 4 should have the highest mean levels of sulfate since it has the lowest mean ANC. However, this was not observed at Site 4 rather it had the lowest mean sulfate and ANC

concentration. Another source of depressed ANC is indicated and likely can be attributed to Anakeesta geology.

From Robinson et al. (2003) stream survey site 52 samples had median concentrations of 13.59, 21.98, 47.08 μeq/l for chloride, nitrate, and sulfate, respectively. Site 1 samples had very similar chloride and nitrate median concentrations. However, Site 1 samples had a median sulfate concentration 9.87 μeq/l lower than site 52 median sulfate concentrations. This is consistent with median stream ANC being higher for Site 1 samples noted in section 3.2. This further indicates acid deposition as the cause for depressed stream ANC and that a decrease in SO_x may improve base flow ANC.

3.4 Metals

Descriptive statistics for base flow metals data are shown in Table 4-8. The given range in Table 4-8 for calcium and magnesium was converted to hardness (mg/l as $CaCO_3$). The range was 3.22 – 7.34 for Site 1, 2.45 – 9.58 for Site 2, 3.07 – 7.74 for Site 3, and 2.44 – 5.32 for Site 4. The mean hardness was 4.83, 4.87, 4.50, 3.59 mg/l as $CaCO_3$ for Site 1 – 4, respectively. Low hardness can cause problems for aquatic life since hardness can help offset acidification problems. At a hardness of 5 mg/l as $CaCO_3$, EPA CCC is 0.00070 mg/l for copper and 0.0093 mg/l for zinc. The mean for all sites exceeded the CCC for both metals. The CCC is 0.087 mg/l for aluminum and 1 mg/l for iron. The mean concentration of either metal did not exceed the CCC. However, there were some exceedances for aluminum which will be discussed in future sections along with copper and zinc exceedances.

Table 4-8. Stream base flow descriptive statistics for cations.

	Al (mg/l)	Ca (mg/l)	Cu (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Mn (mg/l)	Na (mg/l)	Si (mg/l)	Zn (mg/l)
Site 1 (10-6-03 - 5-25-04)										
Maximum	0.150	1.970	0.030	0.050	0.590	0.590	0.010	1.440	3.550	0.040
Q_3	0.050	1.495	0.010	0.020	0.525	0.368	0.005	1.015	2.877	0.019
Median	0.030	1.355	0.000	0.010	0.415	0.335	0.000	0.885	2.615	0.010
Q_1	0.010	1.240	0.000	0.010	0.285	0.260	0.000	0.823	1.868	0.000
Minimum	0.000	1.010	0.000	0.000	0.197	0.170	0.000	0.660	0.140	0.000
Range	0.150	0.960	0.030	0.050	0.393	0.420	0.010	0.780	3.410	0.040
IQR	0.040	0.255	0.010	0.010	0.240	0.108	0.005	0.193	1.010	0.019
Mean	0.038	1.390	0.004	0.014	0.403	0.332	0.002	0.938	2.318	0.011
Std Dev	0.037	0.252	0.008	0.013	0.121	0.093	0.004	0.189	0.865	0.012
N	24	24	20	24	24	24	24	24	24	24
Site 2 (10-6-03 - 5-25-04)										
Maximum	0.120	2.570	0.040	0.090	0.930	0.770	0.010	1.910	3.250	0.100
Q_3	0.050	1.623	0.011	0.033	0.643	0.390	0.000	1.090	3.052	0.030
Median	0.034	1.343	0.007	0.020	0.407	0.330	0.000	0.950	2.870	0.010
Q_1	0.018	1.200	0.000	0.010	0.290	0.258	0.000	0.868	2.549	0.000
Minimum	0.000	0.670	0.000	0.000	0.210	0.190	0.000	0.620	0.120	0.000
Range	0.120	1.900	0.040	0.090	0.720	0.580	0.010	1.290	3.130	0.100
IQR	0.033	0.423	0.011	0.023	0.353	0.133	0.000	0.222	0.503	0.030
Mean	0.036	1.401	0.008	0.023	0.471	0.334	0.001	1.026	2.604	0.019
Std Dev	0.029	0.365	0.010	0.021	0.213	0.118	0.003	0.276	0.791	0.024
N	26	26	21	26	26	26	26	26	26	26
Site 3 (10-6-03 - 5-25-04)										
Maximum	0.300	2.014	0.044	0.293	6.453	0.659	0.017	1.605	4.591	0.115
Q_3	0.073	1.452	0.020	0.052	0.566	0.340	0.006	0.962	2.672	0.025
Median	0.040	1.258	0.009	0.017	0.429	0.307	0.002	0.866	2.373	0.017
Q_1	0.022	1.067	0.000	0.008	0.347	0.247	0.000	0.717	1.809	0.002
Minimum	0.000	0.901	0.000	0.000	0.197	0.200	0.000	0.588	0.073	0.000
Range	0.300	1.113	0.044	0.293	6.256	0.459	0.017	1.017	4.518	0.115
IQR	0.052	0.386	0.020	0.044	0.219	0.093	0.006	0.245	0.863	0.023
Mean	0.063	1.284	0.012	0.042	0.828	0.314	0.003	0.890	2.161	0.019
Std Dev	0.074	0.274	0.013	0.068	1.296	0.099	0.004	0.232	1.030	0.023
N	25	25	20	25	25	25	25	25	25	25
Site 4 (10-6-03 - 5-25-04)										
Maximum	0.183	1.568	0.094	0.187	0.947	0.341	0.016	1.170	3.422	0.086
Q_3	0.156	1.435	0.094	0.158	0.856	0.313	0.014	1.137	3.185	0.073
Median	0.060	0.973	0.007	0.048	0.549	0.212	0.006	0.899	2.306	0.028
Q_1	0.012	0.840	0.000	0.016	0.336	0.120	0.001	0.622	0.876	0.010
Minimum	0.000	0.818	0.000	0.013	0.277	0.096	0.000	0.575	0.455	0.007
Range	0.183	0.750	0.094	0.174	0.669	0.245	0.016	0.595	2.967	0.079
IQR	0.144	0.595	0.094	0.142	0.520	0.193	0.013	0.515	2.309	0.063
Mean	0.076	1.083	0.034	0.074	0.580	0.215	0.007	0.886	2.122	0.037
Std Dev	0.078	0.336	0.052	0.080	0.277	0.101	0.007	0.268	1.237	0.035
N	4	4	3	4	4	4	4	4	4	4

4. Descriptive Statistics of Storm Event Samples

Samples collected by auto-samplers during precipitation events are considered storm samples. This section will be an overview of descriptive statistics. Further analysis of storm event data will follow in Chapter 5.

4.1 pH

The median and mean are lower for storm samples compared to sonde median and mean values (Table 4-9). Mean stream storm flow pH was from 0.27 to 0.45 pH units lower than stream base flow mean pH. The minimum storm flow pH was also 0.87 to 1.11 pH units lower compared to base flow. This is expected since storm sample represent worst case conditions.

4.2 Acid Neutralizing Capacity

Descriptive statistics for acid neutralizing capacity (ANC) for storm samples collected at Sites 1 – 3 are shown in Table 4-10. The median and mean ANC are lower for storm samples compared to base flow samples. The minimum ANC for all three sites is zero. Stream ANC tends to progress toward zero given a large enough precipitation event. The range compared to baseline is larger due to some samples representing increased ANC at onset of a storm event followed by a decline below baseline ANC. The percent change for median and mean ANC from stream base flow to storm flow is shown in Table 4-11. Sites 1 and 2 had at least 75% reduction in mean and median ANC. Notably, Site 3 had lower percent reductions of stream ANC. This is likely due to the lower base flow mean stream ANC.

Table 4-9. Stream storm flow descriptive statistics for pH.

	Stream Sites		
	Site 1	**Site 2**	**Site 3**
Elevation, ft	1370	1400	1600
Dates	12/17/03 - 9/8/04	9/22/03 - 6/24/04	1/18/04 - 7/31/04
		pH	
Maximum	6.34	6.33	6.34
Q_3	6.11	6.14	5.93
Median	6.04	5.88	5.82
Q_1	5.62	5.62	5.66
Minimum	4.85	5.06	4.73
Range	1.49	1.27	1.61
IQR	0.49	0.51	0.27
Mean	5.85	5.84	5.76
Std Dev	0.35	0.33	0.32
N	76	68	49

Table 4-10. Stream storm flow descriptive statistics for ANC.

	Stream Sites		
	Site 1	**Site 2**	**Site 3**
		ANC (µeq/l)	
Maximum	72.79	113.64	184.44
Q_3	38.04	48.03	24.29
Median	28.80	32.10	17.64
Q_1	16.98	17.44	10.84
Minimum	0.00	0.00	0.00
Range	72.79	113.64	184.44
IQR	21.06	30.59	13.45
Mean	28.86	35.12	26.36
Std Dev	15.59	23.20	33.94
N	73	68	49

Table 4-11. Percent change for anion median and mean from base flow to storm flow.

	ANC (µeq/l)	**Chloride (µeq/l)**	**Nitrate (µeq/l)**	**Sulfate (µeq/l)**
		Site 1		
Median	-77%	27%	29%	20%
Mean	-85%	38%	39%	12%
		Site 2		
Median	-82%	23%	40%	27%
Mean	-75%	41%	38%	24%
		Site 3		
Median	-65%	16%	16%	20%
Mean	-25%	44%	33%	24%

Note: A positive number represents an increase during storm flow.

4.3 Sulfate, Nitrate, and Chloride

Mean and median concentration for sulfate, nitrate, and chloride was higher compared to base flow samples collected (Table 4-11). Higher sulfate and nitrate concentrations in stream storm flow are a symptom of acid deposition. Sulfate, nitrate, and chloride descriptive statistics for storm flow samples are shown in Table 4-12.

4.4 Metals

In general, metals concentrations increased during storm flow compared to base flow (Table 4-13). Mean aluminum concentrations increased from 25 – 59% during stream storm flow. This is another symptom of acid deposition. Notably, mean and median sodium and silicon decreased during stream storm flow.

Metal descriptive statistics are shown in Table 4-14. Mean hardness was 5.5, 5.3, and 5.2 mg/l as $CaCO_3$ for Sites 1 – 3 respectively. The mean hardness and range was larger during storm flow compared to base flow which may be due to leaching of base cations from soils. The mean concentration of zinc and copper exceeded the EPA CCC at Sites 1 and 2. Only Site 2 aluminum mean concentration exceeded the CCC. No iron exceedances occurred.

5. Comparison of Descriptive Statistics for Storm Event Samples at Site 3

Section 4 gave descriptive statistics for all storm samples collected. Direct comparisons between storm events should be done cautiously since varying portions of the hydrograph are represented for each storm. Nevertheless, it is important to understand that each storm is different and that there is considerable variability between species concentrations and stage. To help assess this variability the maximum change in stage and the change in stage from when sampling began to peak stage may be seen in

Table 4-12. Stream storm flow descriptive statistics for anions.

	Stream Sites		
	Site 1	**Site 2**	**Site 3**
		Chloride (µeq/l)	
Maximum	122.81	87.94	78.51
Q_3	19.40	18.55	20.74
Median	16.65	15.60	14.44
Q_1	8.57	13.86	10.36
Minimum	0.00	3.15	2.30
Range	122.81	84.79	76.21
IQR	10.83	4.69	10.38
Mean	17.68	18.84	20.19
Std Dev	15.96	13.86	18.41
N	70	59	48
		Nitrate (µeq/l)	
Maximum	59.98	84.94	96.56
Q_3	34.49	36.87	38.17
Median	27.09	32.22	27.53
Q_1	20.83	20.08	22.47
Minimum	11.11	2.72	5.84
Range	48.87	82.22	90.72
IQR	13.66	16.79	15.70
Mean	29.04	31.90	32.60
Std Dev	11.31	16.35	16.78
N	71	61	49
		Sulfate (µeq/l)	
Maximum	89.13	107.70	137.42
Q_3	53.36	56.75	62.98
Median	46.41	52.26	48.60
Q_1	40.23	38.57	39.86
Minimum	27.46	23.75	23.95
Range	61.67	83.95	113.47
IQR	13.13	18.18	23.12
Mean	47.05	50.74	52.75
Std Dev	11.02	15.45	20.26
N	71	61	49

Table 4-13. Percent change for metal descriptive statistics from base flow to storm flow.

	Al (mg/l)	Ca (mg/l)	Cu (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Mn (mg/l)	Na (mg/l)	Si (mg/l)	Zn (mg/l)
Site 1										
Median	40%	2%	0%	50%	25%	4%	0%	-7%	-39%	0%
Mean	25%	11%	-4%	41%	50%	15%	57%	-11%	-72%	-39%
Site 2										
Median	59%	7%	61%	9%	18%	14%	100%	-23%	-53%	36%
Mean	59%	5%	68%	32%	39%	15%	84%	-27%	-55%	0%
Site 3										
Median	60%	-4%	-129%	-2%	20%	13%	56%	-28%	-34%	-68%
Mean	25%	15%	-10%	-71%	-1%	13%	53%	-28%	-42%	2%

Note: A positive number represents an increase during storm flow.

Table 4-14. Stream storm flow descriptive statistics for cations.

	Al (mg/l)	Ca (mg/l)	Cu (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Mn (mg/l)	Na (mg/l)	Si (mg/l)	Zn (mg/l)
Site 1										
Maximum	0.290	5.170	0.030	0.190	4.430	0.730	0.050	1.433	2.350	0.050
Q_3	0.070	1.645	0.010	0.030	0.700	0.470	0.000	0.900	2.130	0.010
Median	0.050	1.380	0.000	0.020	0.550	0.350	0.000	0.828	1.880	0.000
Q_1	0.005	1.220	0.000	0.010	0.475	0.310	0.000	0.735	0.475	0.000
Minimum	0.000	1.060	0.000	0.000	0.290	0.206	0.000	0.610	0.010	0.000
Range	0.290	4.110	0.030	0.190	4.140	0.524	0.050	0.823	2.340	0.050
IQR	0.065	0.425	0.010	0.020	0.225	0.160	0.000	0.165	1.655	0.010
Mean	0.051	1.564	0.004	0.024	0.810	0.391	0.005	0.847	1.346	0.008
Std Dev	0.050	0.660	0.007	0.027	0.863	0.109	0.013	0.176	0.890	0.011
N	57	57	57	57	57	57	57	57	57	57
Site 2										
Maximum	0.318	2.019	0.101	0.443	5.913	0.627	0.040	2.124	3.116	0.058
Q_3	0.116	1.610	0.037	0.042	0.631	0.441	0.014	0.846	2.180	0.028
Median	0.082	1.447	0.019	0.022	0.500	0.385	0.006	0.773	1.872	0.016
Q_1	0.055	1.300	0.007	0.011	0.449	0.332	0.001	0.651	1.481	0.007
Minimum	0.000	1.092	0.000	0.000	0.305	0.229	0.000	0.565	0.031	0.000
Range	0.318	0.927	0.101	0.443	5.607	0.398	0.040	1.560	3.085	0.058
IQR	0.061	0.309	0.030	0.031	0.182	0.109	0.014	0.195	0.699	0.021
Mean	0.088	1.481	0.025	0.033	0.778	0.391	0.008	0.808	1.676	0.019
Std Dev	0.055	0.225	0.023	0.058	0.964	0.089	0.009	0.265	0.773	0.015
N	60	60	60	60	56	60	60	60	60	60
Site 3										
Maximum	0.178	4.076	0.093	0.165	4.917	0.778	0.063	1.527	2.869	0.087
Q_3	0.120	1.587	0.011	0.028	0.918	0.407	0.007	0.741	1.994	0.034
Median	0.101	1.213	0.004	0.017	0.536	0.351	0.005	0.678	1.766	0.010
Q_1	0.037	1.135	0.000	0.009	0.419	0.282	0.000	0.603	1.531	0.000
Minimum	0.000	1.058	0.000	0.000	0.260	0.142	0.000	0.501	0.002	0.000
Range	0.178	3.018	0.093	0.165	4.656	0.636	0.063	1.026	2.867	0.087
IQR	0.083	0.452	0.011	0.019	0.499	0.125	0.007	0.138	0.463	0.034
Mean	0.083	1.505	0.011	0.024	0.817	0.361	0.007	0.694	1.528	0.019
Std Dev	0.054	0.670	0.019	0.029	0.790	0.126	0.012	0.153	0.737	0.021
N	48	48	48	48	48	48	48	48	48	48

Table 4-15. Descriptive statistics for individual storm events for Site 3 are shown in Table 4-16.

6. Metal Exceedances in Base and Storm Flow Stream Samples

Metal exceedances for copper, zinc, and aluminum are shown in Table 4-17 for base and storm flow samples for Sites 1 – 3. Copper and zinc exceedances were based on the hardness of that particular sample. Aluminum did not exceed the CMC for any samples. However, aluminum did exceed the CCC about 50 – 60% of the time during storm samples and about 25% during base flow. Increased aluminum exceedances during storm flow are another symptom of acid deposition. Copper and zinc had numerous exceedances during base and storm flow.

The total exceedances for CMC for all metals were 33, 49, and 43% for Sites 1 – 3 respectively. This could represent serious water quality problems. However, Hansen et al. (2003) found the zinc LC50 for rainbow trout to be approximately 0.125 mg/l at a pH of 6.5 and hardness of 30 mg/l as $CaCO_3$. The EPA CMC for the given hardness is 0.042 mg/l. The standard must be exceeded by almost three times to reach the LC50 value. This standard is a likely a blanket standard for a diverse ecosystem. Rainbow trout may be unaffected if the standard is exceeded but other organisms may.

Table 4-15. Stage change information for statistics given in Table 4-16.

Storm Event	Max Change in Stage (ft)	Max Change in Stage of Samples Captured (ft)
December 17, 2003	0.554	0.254
January 18, 2004	1.037	0.22
March 6, 2004	**	**
May 2, 2004	1.537	0.268
June 25, 2004	1.218	0.999
July 31, 2004	1.418	0.284

(**Not Available.)

Table 4-16. Descriptive statistics for individual storm event samples at Site 3.

	Lab pH	ANC µeq/l	Nitrate µeq/l	Sulfate µeq/l	Base Cation Sum µeq/l	Al ppm	Cu ppm	Zn ppm
Storm Event				December 17, 2003				
Maximum	6.03	29.63	25.08	54.83	236.67	0.070	0.093	0.068
Median	5.92	24.23	23.23	44.78	128.03	0.000	0.046	0.040
Minimum	5.88	18.19	21.11	39.52	109.60	0.000	0.034	0.000
Mean	5.95	23.31	23.29	45.56	162.91	0.014	0.058	0.032
Std Dev	0.08	4.53	1.54	6.33	63.39	0.031	0.028	0.030
N	5	5	5	5	5	5	5	5
Storm Event				January 18, 2004				
Maximum	6.03	24.76	61.14	78.86	148.91	0.175	0.035	0.055
Median	5.86	18.60	28.54	46.31	136.13	0.121	0.004	0.032
Minimum	5.69	16.00	20.29	32.09	120.59	0.000	0.002	0.015
Mean	5.86	18.66	30.87	47.76	135.10	0.108	0.008	0.032
Std Dev	0.10	2.75	12.11	12.72	11.58	0.050	0.010	0.012
N	9	9	9	9	9	9	9	9
Storm Event				March 6, 2004				
Maximum	5.75	18.60	67.17	78.77	330.43	0.127	0.000	0.052
Median	5.67	10.40	46.43	59.16	213.80	0.023	0.000	0.009
Minimum	4.73	0.00	37.28	48.60	154.13	0.000	0.000	0.000
Mean	5.42	8.74	43.48	58.86	229.60	0.018	0.000	0.014
Std Dev	0.43	6.94	9.24	9.39	62.42	0.040	0.000	0.018
N	10	10	10	10	10	10	10	10
Storm Event				May 2, 2004				
Maximum	6.28	29.34	96.56	137.42	169.05	0.118	0.023	0.010
Median	5.87	16.29	35.67	70.49	133.12	0.101	0.006	0.003
Minimum	5.72	10.53	27.30	62.76	124.37	0.067	0.000	0.000
Mean	5.89	17.06	45.75	81.00	136.83	0.096	0.005	0.004
Std Dev	0.18	6.19	25.04	24.21	14.24	0.019	0.008	0.005
N	8	7	8	8	8	8	8	8
Storm Event				June 25, 2004				
Maximum	5.92	26.96	52.83	55.36	141.37	0.178	0.011	0.087
Median	5.55	11.15	22.47	40.22	126.63	0.118	0.004	0.019
Minimum	5.43	6.92	15.37	27.66	120.56	0.112	0.001	0.000
Mean	5.64	14.73	25.02	41.21	128.20	0.134	0.005	0.026
Std Dev	0.19	7.56	11.25	9.19	6.14	0.026	0.003	0.026
N	10	10	10	10	10	10	10	10
Storm Event				July 31, 2004				
Maximum	6.34	184.44	55.62	82.45	283.13	0.131	0.014	0.053
Median	6.17	82.78	16.12	27.04	164.34	0.078	0.012	0.003
Minimum	5.94	36.61	5.84	23.95	140.46	0.062	0.009	0.000
Mean	6.15	97.57	20.52	39.65	183.49	0.088	0.011	0.012
Std Dev	0.15	56.95	17.79	23.60	53.71	0.027	0.002	0.021
N	6	6	6	6	6	6	6	6

Table 4-17. Metal Exceedances for Stream Sites 1 – 3.

	Site 1													
	Storm Flow						Base Flow						Total Exceedances	
	Aluminum		Copper		Zinc		Aluminum		Copper		Zinc			
	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC
# exceedances	0	10	38	38	16	16	0	2	13	13	12	12	79	91
# events	57	57	57	57	57	57	24	24	20	20	24	24	239	239
% exceedance	0	18	67	67	28	28	0	8	65	65	50	50	33	38
	Site 2													
	Storm Flow						Base Flow						Total Exceedances	
	Aluminum		Copper		Zinc		Aluminum		Copper		Zinc			
	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC
# exceedances	0	28	55	55	39	39	0	2	15	15	16	16	125	155
# events	60	60	60	60	60	60	26	26	21	21	26	26	253	253
% exceedance	0	47	92	92	65	65	0	8	71	71	62	62	49	61
	Site 3													
	Storm Flow						Base Flow						Total Exceedances	
	Aluminum		Copper		Zinc		Aluminum		Copper		Zinc			
	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC
# exceedances	0	25	36	36	28	28	0	4	13	13	16	16	93	122
# events	49	49	49	49	49	49	25	25	20	20	25	25	217	217
% exceedance	0	51	73	73	57	57	0	16	65	65	64	64	43	56

7. Analysis of Precipitation Samples

Precipitation water quality is a controlling factor of stream water quality and thus it is prudent to present an overview of precipitation water quality. As discussed in Chapter 3, precipitation samples were collected by two methods: bulk collector and a sequential collector. The bulk collector collected a large volume of precipitation that was exposed to the environment until collection. The sequential collector partitioned samples into capped 50 ml bottles. The two different collection methods resulted in varying precipitation water quality.

7.1 pH Descriptive Statistics

The median pH was 4.88 and 4.37 for sequential and bulk collection respectively (Table 4-18). Mean pH was 4.99 and 4.49 for sequential and bulk collection respectively. The differences in median and mean are likely due to the differences in sample collection method. Bulk precipitation samples are exposed to the environment and collected every two weeks. However, sequential samples are kept in capped bottles and are not exposed to sunlight. Also, sequential samples were collected within two days of collection. The mean pH for both collection methods was lower than mean stream pH for all sites.

Table 4-18. Precipitation descriptive statistics for pH.

	Sequential	Bulk
	pH	
Maximum	6.03	5.49
Q_3	5.42	4.71
Median	4.88	4.37
Q_1	4.56	4.15
Minimum	3.93	3.99
Range	2.10	1.50
IQR	0.86	0.56
Mean	4.99	4.49
Std Dev	0.59	0.40
N	43	24

7.2 Anions Descriptive Statistics

The median ANC was 0 μeq/l for both collection methods (Table 4-19). However, the mean ANC for sequential collection was 20.87 μeq/l compared to 0.43 μeq/l for bulk collection. The high ANC values typically seen in the first collection bottle skews the data pulling the mean away from the median for sequential collection. The range for the remaining anions was wider for sequential collection. The mean sulfate concentration in precipitation was higher than mean stream base flow and comparable to stream storm flow mean concentrations. Chloride and nitrate also followed this general trend. This further indicates the strong relationship precipitation has on stream water quality.

7.3 Metals Descriptive Statistics

Metals descriptive statistics are shown in Table 4-20. In general, mean concentrations of precipitation tended to be lower than stream samples. A notable difference was seen in the sequential precipitation mean zinc concentration. Mean sequential precipitation for zinc was 0.179 mg/l while Site 3 mean was 0.019 mg/l for storm flow. Aluminum did not exceed the CCC for either collection method. This indicates the increased storm flow exceedances are due to soil sources.

7.4 Temporal Variation in Precipitation Chemistry

The sequential precipitation collector allowed analysis of temporal change in precipitation chemistry. Several studies had document changes in precipitation chemistry over time (Semonin 1976, Seymour et al. 1976, and Railsback 1997). Precipitation pH varied from 4.31 to 5.85 for a storm event beginning 9/6/2004 (Figure 4-15). pH was highest in the first sample collection for this storm event and is the general trend for

Table 4-19. Precipitation descriptive statistics for anions.

	ANC (µeq/l)	Chloride (µeq/l)	Nitrate (µeq/l)	Sulfate (µeq/l)
	Bulk Precipitation Samples (10/16/03 - 9/15/04)			
Maximum	9.91	14.57	144.12	231.47
Q_3	0.00	7.67	32.45	44.69
Median	0.00	5.73	19.58	36.98
Q_1	0.00	1.63	7.59	15.28
Minimum	0.00	0.00	0.00	8.30
Range	9.91	14.57	144.12	223.17
IQR	0.00	6.03	24.86	29.41
Mean	0.43	5.46	30.36	51.21
Std Dev	2.02	4.36	35.33	58.72
N	24	23	24	24
	Sequential Precipitation Samples (11/7/03 - 9/9/04)			
Maximum	143.72	65.40	187.02	332.40
Q_3	12.41	12.53	20.98	51.63
Median	0.00	5.40	11.37	32.14
Q_1	0.00	3.19	6.30	14.38
Minimum	0.00	0.00	0.00	5.56
Range	143.72	65.40	187.02	326.84
IQR	12.41	9.34	14.68	37.25
Mean	20.87	9.24	27.72	55.75
Std Dev	40.95	11.95	41.90	70.97
N	43	36	36	36

Table 4-20. Precipitation descriptive statistics for cations.

	Al (mg/l)	Ca (mg/l)	Cu (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Mn (mg/l)	Na (mg/l)	Si (mg/l)	Zn (mg/l)
Bulk Precipitation Samples										
Maximum	0.083	1.358	0.021	0.065	0.957	0.141	0.012	0.442	0.417	0.088
Q_3	0.051	0.623	0.006	0.020	0.610	0.058	0.008	0.307	0.173	0.037
Median	0.013	0.412	0.002	0.016	0.305	0.026	0.001	0.252	0.035	0.020
Q_1	0.000	0.274	0.000	0.009	0.207	0.000	0.000	0.194	0.000	0.000
Minimum	0.000	0.191	0.000	0.000	0.113	0.000	0.000	0.000	0.000	0.000
Range	0.083	1.167	0.021	0.065	0.843	0.141	0.012	0.442	0.417	0.088
IQR	0.013	0.221	0.002	0.016	0.192	0.026	0.001	0.252	0.035	0.020
Mean	0.028	0.522	0.004	0.019	0.391	0.039	0.004	0.237	0.095	0.024
Std Dev	0.029	0.339	0.006	0.018	0.251	0.041	0.005	0.125	0.145	0.025
N	19	19	15	19	19	19	19	19	19	19
Sequential Precipitation										
Maximum	0.050	4.443	0.052	0.058	1.091	0.316	0.030	0.628	0.352	0.527
Q_3	0.021	1.637	0.011	0.017	0.467	0.043	0.006	0.331	0.215	0.310
Median	0.000	0.590	0.000	0.007	0.295	0.007	0.000	0.233	0.035	0.130
Q_1	0.000	0.378	0.000	0.000	0.207	0.000	0.000	0.196	0.003	0.054
Minimum	0.000	0.121	0.000	0.000	0.076	0.000	0.000	0.000	0.000	0.000
Range	0.050	4.322	0.052	0.058	1.015	0.316	0.030	0.628	0.352	0.527
IQR	0.000	0.469	0.000	0.007	0.219	0.007	0.000	0.233	0.035	0.130
Mean	0.011	1.111	0.008	0.011	0.389	0.040	0.004	0.261	0.096	0.179
Std Dev	0.016	1.119	0.014	0.014	0.269	0.072	0.007	0.129	0.117	0.157
N	29	29	23	29	29	29	29	29	29	28

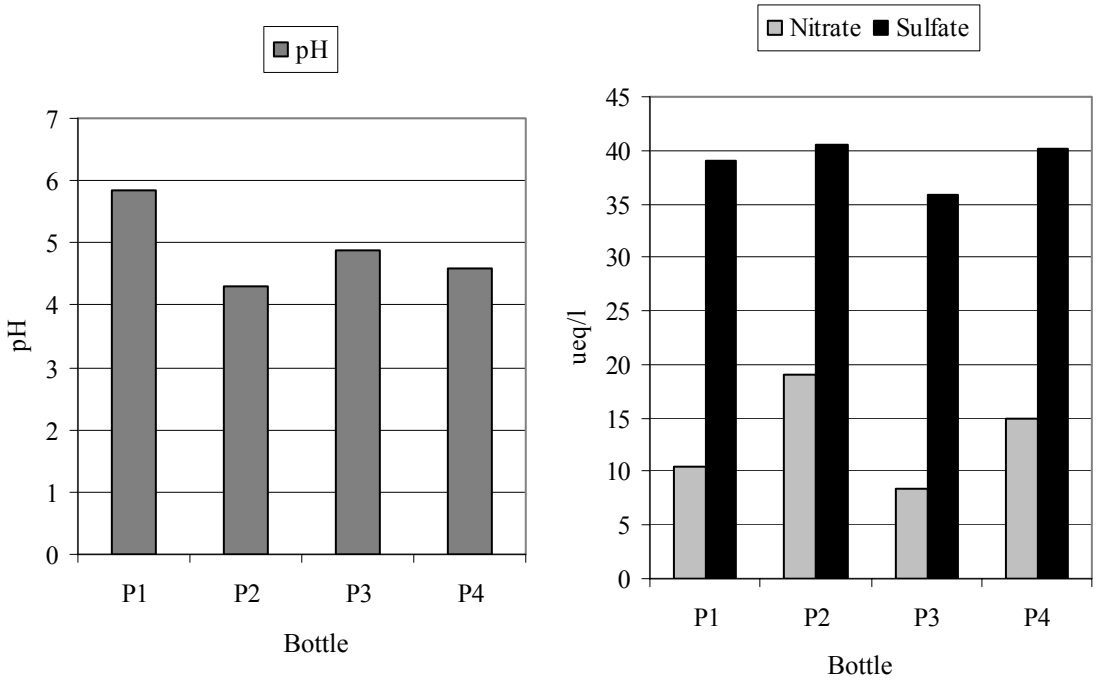

Figure 4-15. Temporal variability in pH, nitrate, and sulfate for 9/6/2004 event.

all storm events. pH varied between 4.31 to 4.88 after the first sample. Sulfate and nitrate also varied during the storm event. A slight pattern was apparent. Sample two (P2) had the highest concentration of sulfate and nitrate, sample four the second highest concentration of sulfate and nitrate, sample one the third highest, and sample three the fourth highest (Figure 4-15). This indicates that sources of nitrate and sulfate are linked. Other parameters also exhibited variation.

7.5 Spatial Variation in Precipitation Chemistry

Temporal variation was apparent in the Figure 4-15. Statistical methods were also used to assess spatial variation between Site 5 (elev. 1440 feet) and 6 (elev. 2240) precipitation sites. The sites are approximately three miles apart. Bulk and sequential precipitation samples were collected at both sites. The two methods of collection were considered separate. Three constituents will be used to assess variability: pH, nitrate, and sulfate.

Box plots were constructed for each constituent for bulk precipitation (Figure 4-16). Visual inspection illustrates variation in each constituent. The Tukey Method which tests the mean by pair wise differences of $y_{max} - y_{min}$ was used to determine significant variation. Neither pH, nitrate, nor sulfate were statistically different. To confirm this, a Wilcoxon rank-sum nonparametric test was employed. No statistical difference was shown between sites for these constituents.

Next, sequential precipitation pH, nitrate, and sulfate box plots were constructed (Figure 4-17). Again some variation was apparent from visual inspection. Employing the same tests, pH, nitrate, and sulfate were not found to be statistically different between

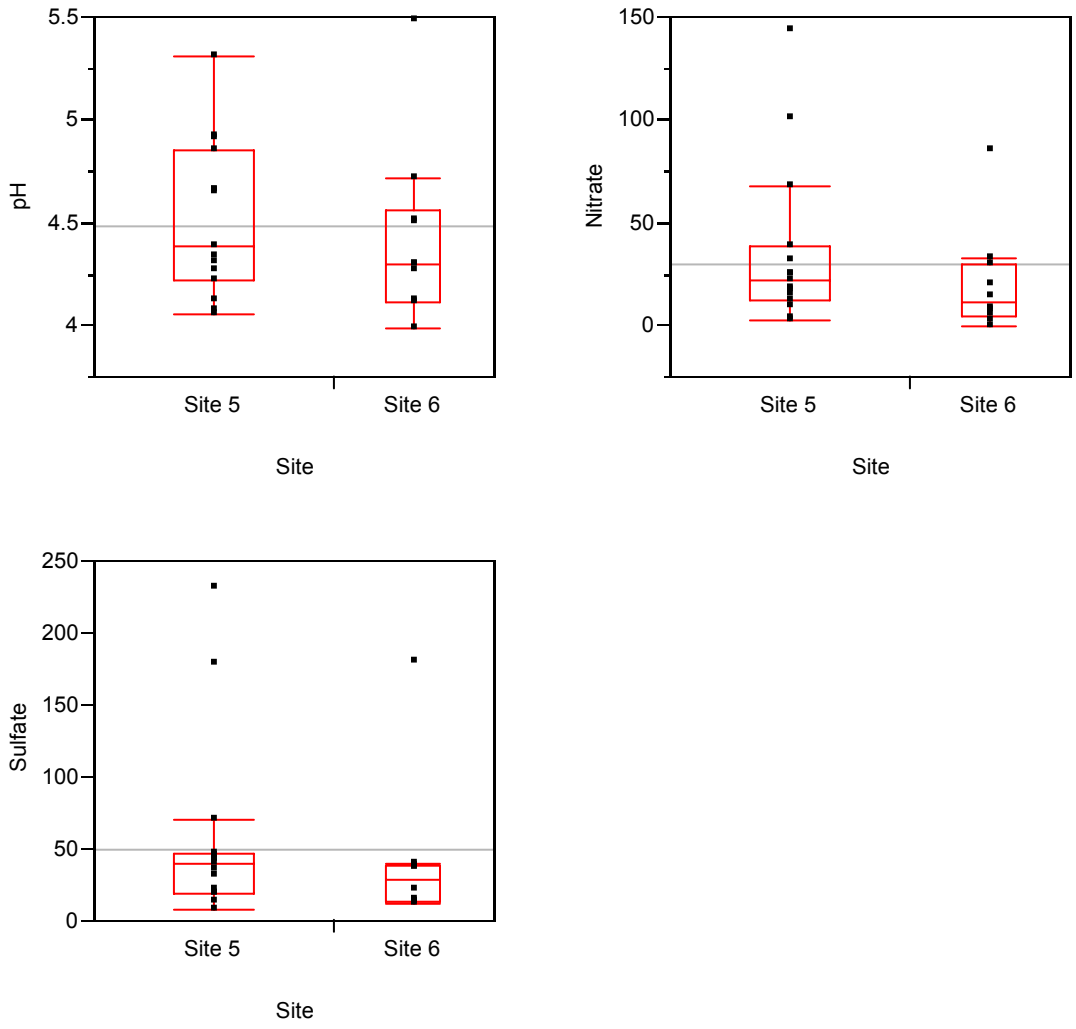

Figure 4-16. Box plots for bulk precipitation pH, nitrate, and sulfate (mean of combined samples displayed as straight, horizontal line).

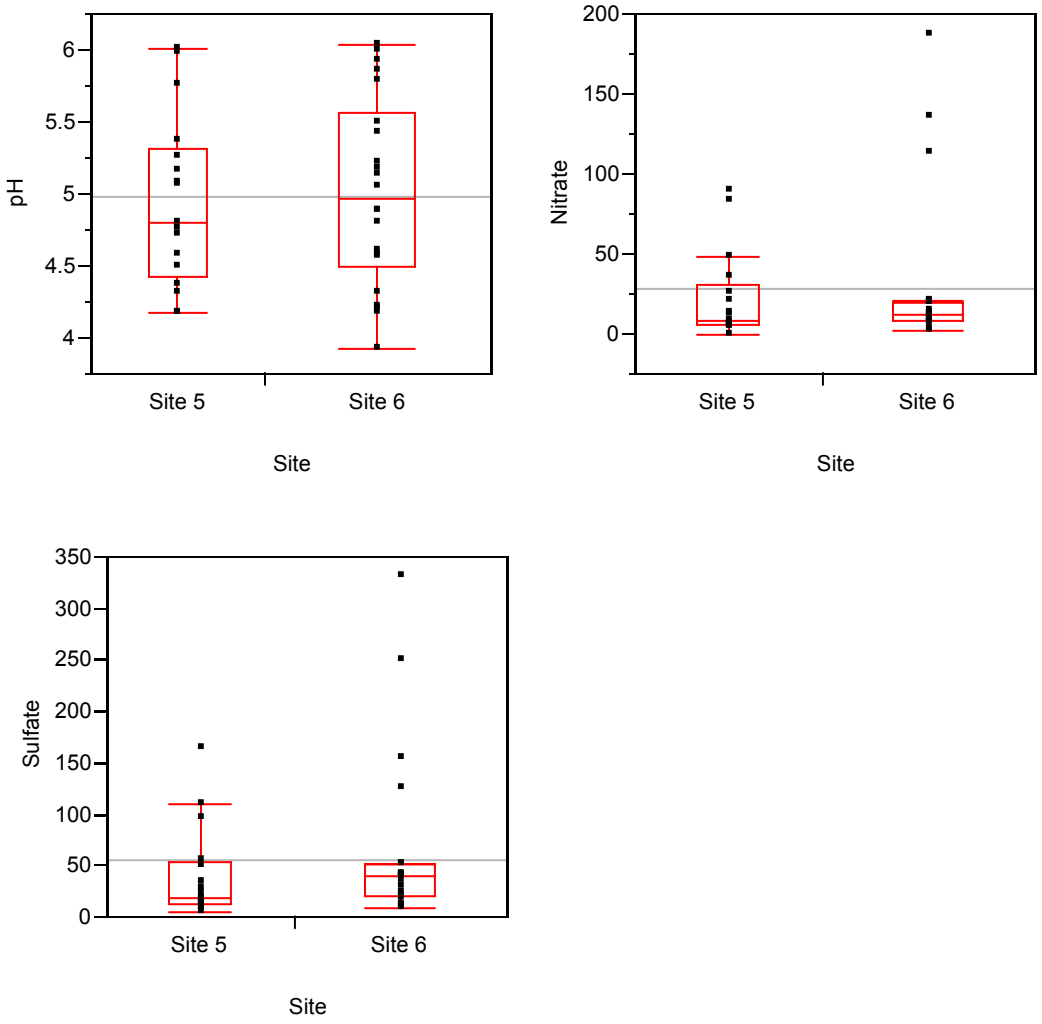

Figure 4-17. Box plots for sequential precipitation pH, nitrate, and sulfate (mean of combined samples displayed as straight, horizontal line).

Sites 5 and 6. No spatial variability was found between Sites 5 and 6 using either collection method.

8. Comparison of pH at Sites 1 – 3

The major objectives of this study were to establish a basis of comparison for pre-construction, construction, and post construction data and to gain further insight into the watershed dynamics. With these objectives in mind it seems prudent to first establish if there is a difference in water quality between the sites that may be affected by construction activities. This should also further the understanding of water quality variability. pH was selected as an indicator of differences between the sites. Stream sonde and laboratory pH will be used. Notably, the statistical methodology used in the analyses below provide a template for comparing water quality between the different stages of construction in order to detect any construction impacts.

8.1 Sonde pH Statistical Comparison

8.1.1 Q-Q plots

Quantile-quantile plots provide an initial graphical method of assessing any differences between sites and are a valuable first step into conducting hypothesis testing (Helsel and Hirsh 1992). A Q-Q plot is constructed by first ranking the data then plotting the ranked data as a scatter plot. If the data are from the same distribution then a straight line (Y=X) should be approximated (Helsel and Hirsh 1992). Figure 4-18 indicates that all three sites differ significantly from a Y=X straight line indicating differences between each site.

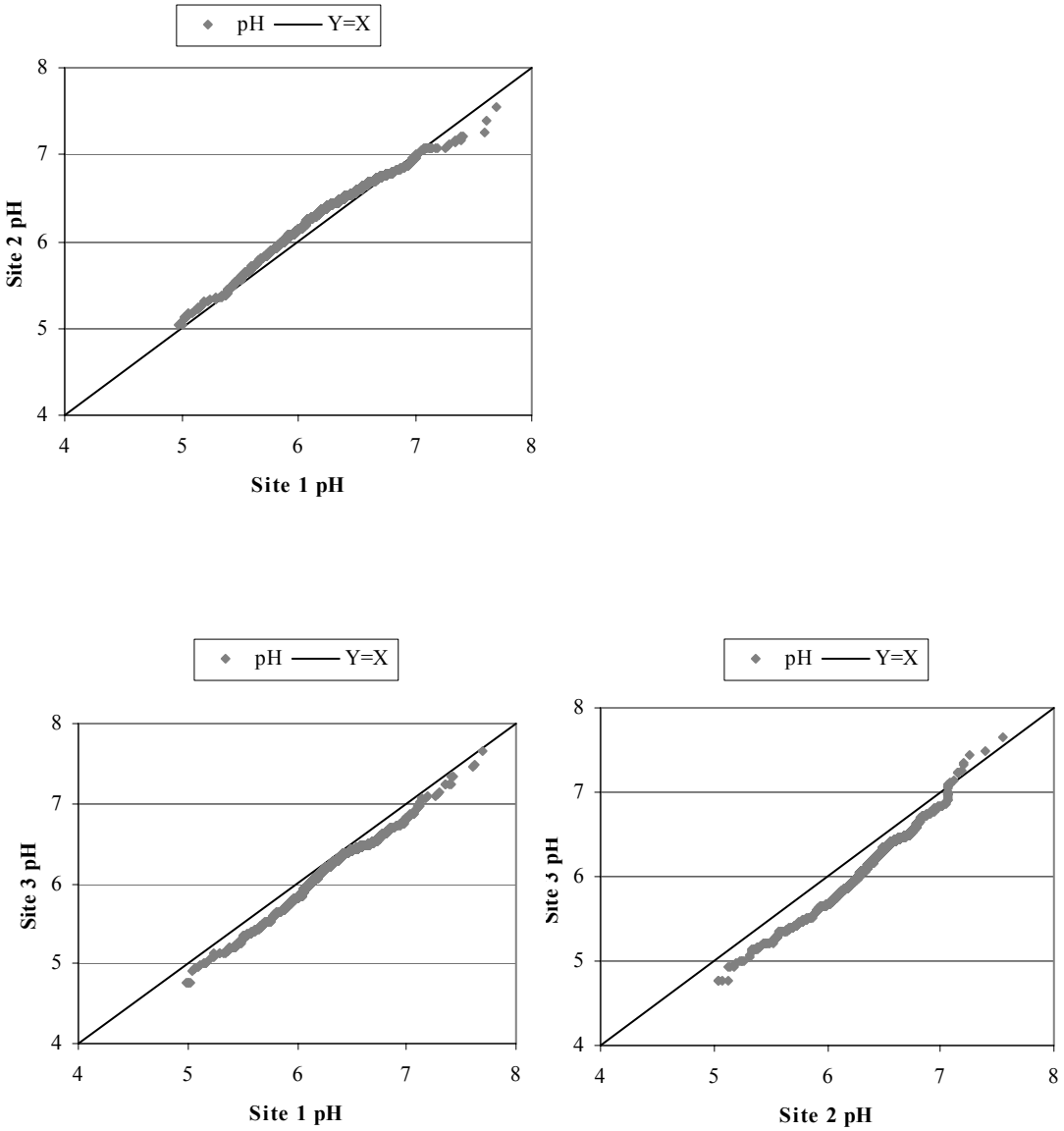

Figure 4-18. Q-Q plot for sonde pH data at Sites 1 – 3.

8.1.2 Wilcoxon Signed-Ranks Test

The Q-Q plots indicated a difference in pH at each site. A formal hypothesis test will be used to confirm or refute the plots. The sonde data were divided into seasonal data sets based on the premise provided by Harwell (2001), who divided the data into four groups to represent seasonal effects. The four groups are December – April, May – June, July – September, and October – November. This division of data served two purposes. It allowed the data to be divided into a logical smaller set. If a data set is large enough then statistically significant differences between the sites would inevitably be found. Also, it helped to eliminate differences that may be only due to seasonal differences. Importantly, the sonde logged pH every fifteen minutes which raises the possibility that a time delay of water quality may be present and effect some statistical test such as paired differences. However, peak stages in all the storms investigated showed peak stage occurred at all three sites within fifteen minutes of each other. Thus any time delay was deemed negligible.

The pH data were not normally distributed (Figure 4-5) and a nonparametric test was chosen to assess any differences. The Wilcoxon signed-ranked test is a nonparametric test that determines if the median difference between paired observations equals zero (Helsel and Hirsh 1992). The null hypothesis is that the median difference is equal to zero and p-values less than 0.05 gives evidence against the null. All sites have statistical evidence that their median pH is significantly different (Table 4-21). The mean differences in Table 4-21 indicate that Site 2 and Site 3 tend to differ the most. The median pH of Site 1, 2 and 3 was 6.45, 6.53, and 6.38, respectively. The median varies the most between Site 2 and 3 and thus it is expected that their mean differences be

Table 4-21. P-values and mean difference for the Wilcoxon signed rank test for Site 1 – 3.

	Sept. 2003		Oct. - Nov. 2003		Dec. - April 2003		May - June 2004		July - Aug. 2004	
	p-value	Mean difference	p-value	Mean difference	p-value	Mean difference	p-value	Mean difference	p-value	Mean difference
Site 1 - Site 2	0.0000	-0.008	0.0020	0.009	0.0000	-0.115	0.0000	-0.099	0.0000	-0.073
Site 2 - Site 3	0.0000	0.216	0.0000	0.215	0.0000	0.157	0.0000	0.206	0.0000	0.205
Site 1 - Site 3	0.0000	0.002	0.0000	0.224	0.0000	0.041	0.0000	0.107	0.0000	0.132

higher as well. The mean differences also indicate that Site 2 tends to be slightly higher than Site 1. Figure 4-19 helps to identify if a site has consistently higher or lower differences. If the straight line (mean difference) is toward one site than it indicates that site tends to be higher. The difference between Site 1 and 2 is less pronounced. This is expected since the sites are close in elevation and less than one mile from each other. Site 1 stream pH tended to be higher than Site 3.

8.2 Baseline Grab pH Comparison

The sonde pH data proved that there are water quality differences between Sites 1 – 3 but these data included storm events. A difference in storm event water quality does not necessarily mean that there are differences during base flow. To evaluate base flow differences between the stream sites, grab samples collected during base flow were compared. The mean pH for Site 1, 2, and 3 was 6.25, 6.29, and 6.03 respectively. The distribution of Site 1 and 2 seem to very close as indicated by the box plot seen in Figure 4-20. Site 3 seems to be significantly lower. A formal hypothesis test was used to test if the mean of the three sites are significantly different. The data were normally distributed as indicated by a goodness of fit test ($p = 0.7219$) and an independent group t-test was used with the null being that the means are equal. Any value p-value below 0.05 gives evidence against the null. The mean of Sites 1 and 2 was not statistically different (Table 4-17). Site 3 was statistically different from Sites 1 and 2. A matched pair t-test was also employed to determine any differences between the median pH. A matched pair test can be more powerful in detecting differences since it blocks out variability by only looking at the differences of the measurements (Helsel and Hirsh 1992). The t-test indicates that all three sites have statistically different median pH although the mean difference

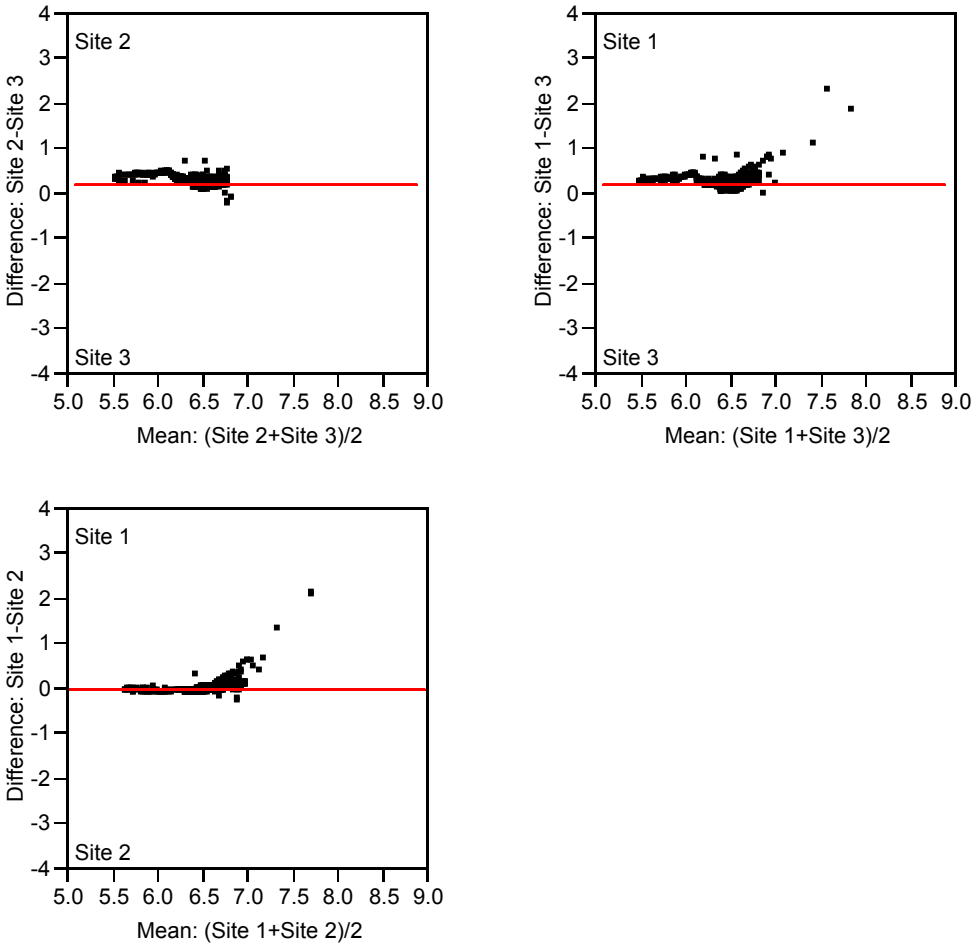

Figure 4-19. Plotted differences of Sites 1 – 3 with mean difference plotted as straight line (September 2003 data set).

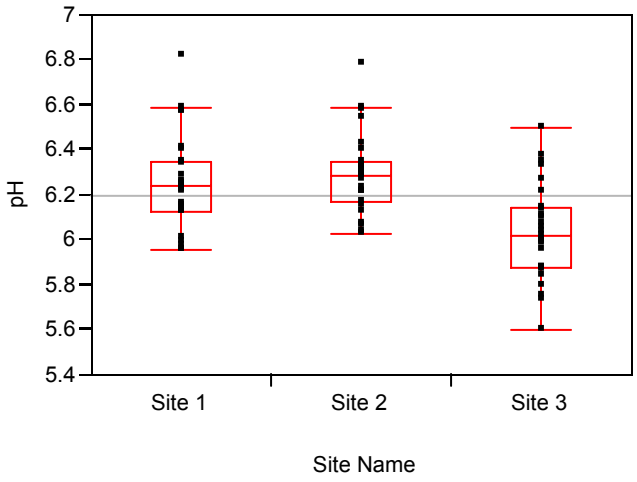

Figure 4-20. Box plot for baseline grab samples laboratory pH at Sites 1 – 3.

between Site 1 and 2 is close to zero (Table 4-22). As with the sonde pH, Site 2 pH tends to be higher than Sites 1 and 3.

8.3 Summary

There are several other parameters that could be used to evaluate differences between the three steam sites. However, pH is a very good indicator of differences due to its dominate role compared to other parameters. It was found that each site statistically varied using sonde and baseline grab sample pH. The only exception was that the mean pH of Site 1 and 2 were not significantly different. In all cases Site 2 tended to have higher pH values. This is somewhat consistent with past research since Site 3 is at a higher elevation (Barnett 2003). However, Site 1 is at a lower elevation and its pH should tend to be higher. The elevation difference is slight and other factors may cause the discrepancy.

9. Conclusions

Conclusions drawn from this chapter are:

- Stream base flow mean pH based on sonde and grab samples for aquatic habitats was acceptable at Sites 1 – 3. Low stream mean base flow pH at Site 4 indicates problems with chronic acidification.
- Minimum sonde pH is about 5.0 for Sites 1 – 3 and 4.0 for Site 4. This indicates problems with acute episodic acidification at all four stream sites. However, Sites 1 – 3 spent very little time (less than 1% of total time) at sonde stream pH less than 5.5. Lower mean pH for storm flow compared to base flow grab samples also indicates episodic acidification was present.

Table 4-22. Results of mean and median hypothesis testing.

	p-values for t-test		
	Mean test	Median test	Mean Difference
Site 1 / Site 2	0.4816	0.0001	-0.039
Site 2 / Site 3	0.0000	<0.0001	0.260
Site 1 / Site 3	0.0001	<0.0001	0.221

- Sites 1 and 2 stream water ANC during base flow was acceptable (Table 4-7). Site 3 stream water ANC was potentially sensitive to episodic acidification. Site 4 stream water ANC indicated high sensitivity to acute episodic acidification.
- Sites 1 – 3 had minimum stream ANC values of zero during storm flow. Mean stream ANC decreased 25 – 85% during stream storm flow compared to base flow.
- Elevated nitrate and sulfate during storm flow are a symptom of acid deposition. Mean sulfate and nitrate concentrations increased 12 – 39% during storm flow compared to base flow.
- Mean sulfate concentration in precipitation was about 50 μeq/l for both collection methods. Notably, Sites 1 – 3 had mean sulfate concentrations of about 50 μeq/l during storm flow. Similar results were observed for nitrate. Chloride mean concentration was lower in precipitation compared to stream storm flow.
- Metals mean concentrations generally increased during storm flow. Aluminum concentrations increased 25 – 59% during storm flow. Notably, sodium and silicon mean concentrations decreased 11 – 72%.

- A number of metal exceedances occurred at Sites 1 – 3. Aluminum exceedances increased during storm flow above concentrations present in precipitation samples indicating soil leaching. Copper and zinc had numerous exceedances during base and storm flow due to low hardness of LPR water.
- Turbidity levels reached levels over 1000 NTU at Sites 1 – 3. However, very little time (3.73 days out of 321.5 days for Site 2) was spent over turbidity of 25 NTU.
- Sonde temperature readings indicated acceptable temperature ranges for brook and rainbow trout at all stream sites.
- Precipitation water quality exhibited temporal but not spatial variability.
- Sites 1 – 3 had statistically different base flow and sonde stream pH. One exception was found when comparing the mean base flow pH at Site 1 and 2.

Chapter V. Analysis of Storm Event Water Quality

1. Introduction

Baseline stream pH in the LPR watershed and other waters of the GRSM are good. Approximately 78% of base flow grab samples taken as part of the GRSM stream survey from October 1993 to November 2002 had median pH above 6.0 (Robinson et al. 2003). Contrasting with base flow, storm event water quality has been shown to have the worst water quality but has received little attention in the GRSM compared to the amount of data collected during base flow conditions. This study provided a chance to study storm event water quality through the use of sondes and auto-samplers.

2. Case Study of a Single Storm Event

This section will present a detailed overview of a storm event beginning on July 25, 2004 at Site 3. This section will provide a general guideline for how stream water quality varies during storm events but does not describe all storm events. Precipitation (Figure 5-1) resulted in run-off and a consequent rise in stage. Based on rain gauges and sonde data, approximately one inch of precipitation resulted in a one foot increase in stage at Site 3 (Figure 5-2). The behavior of pH, anions, cations, conductivity, turbidity, and temperature during this increased stage will be discussed.

2.1 pH Behavior

Increased stage generally causes a depression in stream pH as shown in Figure 5-2. Almost all storm events result in depressed stream pH. This storm event caused a stream pH drop of 0.8 units. Additionally, it is a common occurrence for the minimum

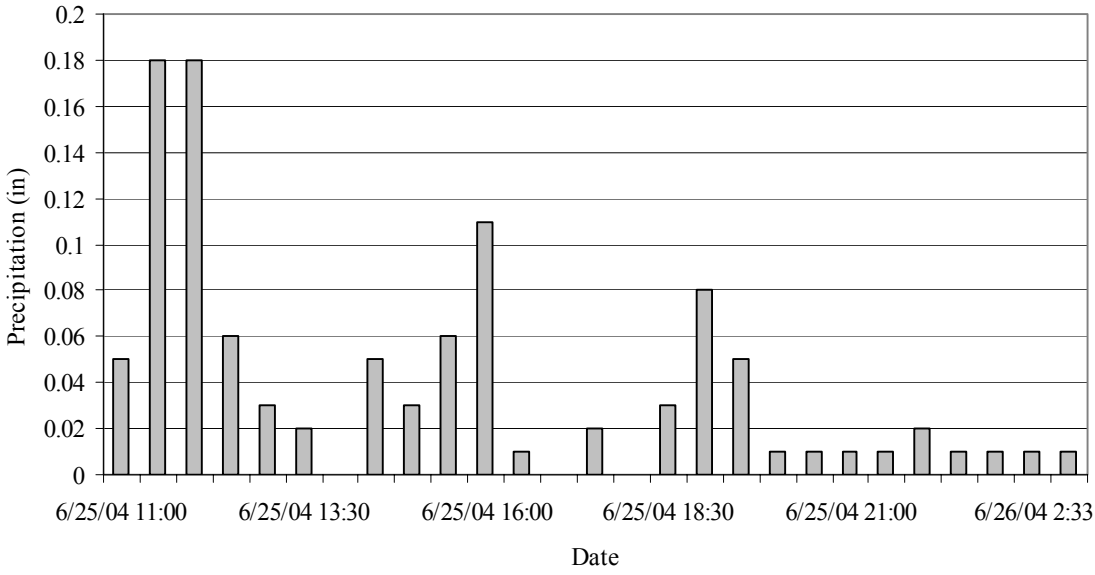

Figure 5-1. Storm event precipitation recorded at Site 5. Total Volume was 1.06 inches. Bars represent 15-minute cumulative values in inches.

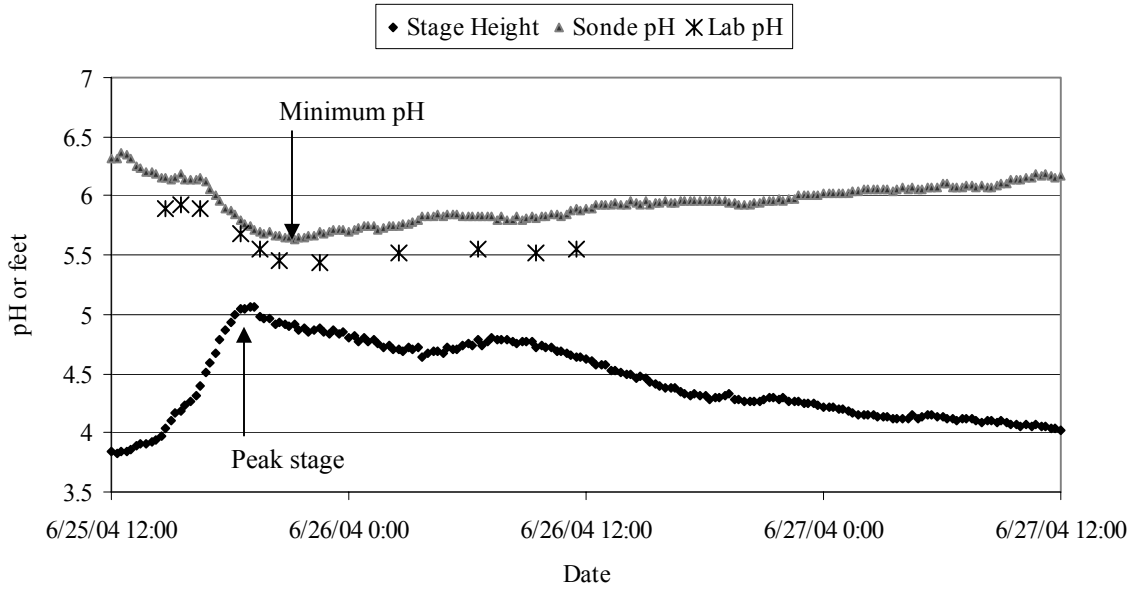

Figure 5-2. Storm event at Site 3 showing increased stage and depressed pH.

stream pH to be observed after the peak stage. The minimum pH lagged peak stage by two hours for this storm event. Lab pH followed the same trend as sonde pH but is generally lower.

2.2 Anion Behavior

Similar to pH, ANC tends to depress during a storm event and a storm event of sufficient size will cause stream ANC to drop to zero. Mean base flow ANC at Site 3 was 33 μeq/l but ANC is reduced to 7 μeq/l during this storm. Figure 5-3 illustrates that ANC follows stage fairly close. There is s second smaller event that causes stage to rise and again ANC to decrease. Also similar to pH, the minimum ANC is seen after the peak stage.

The dominate anion during storm events is usually sulfate but nitrate is also a major anion. Chloride concentrations tend to be less than sulfate or nitrate. The maximum sulfate and nitrate concentration is seen after peak stage (Figure 5-4). The delay in concentration of anions is likely related to the delay seen in minimum pH since nitrate and sulfate is an indicator of acid input from precipitation. There is another increase in sulfate and nitrate that corresponds with the second smaller rise in stage (Figure 5-4).

2.3 Metals Behavior

The major cations are calcium, magnesium, and sodium. Potassium usually is present in lesser concentrations. The base cations generally also exhibit a delay between maximum concentration and peak stage (Figure 5-5). Iron and manganese also exhibited delayed concentration compared to peak stage. A relationship between the delays in all ions is likely related. However, sodium and silicon had minimum concentrations that occurred after peak stage.

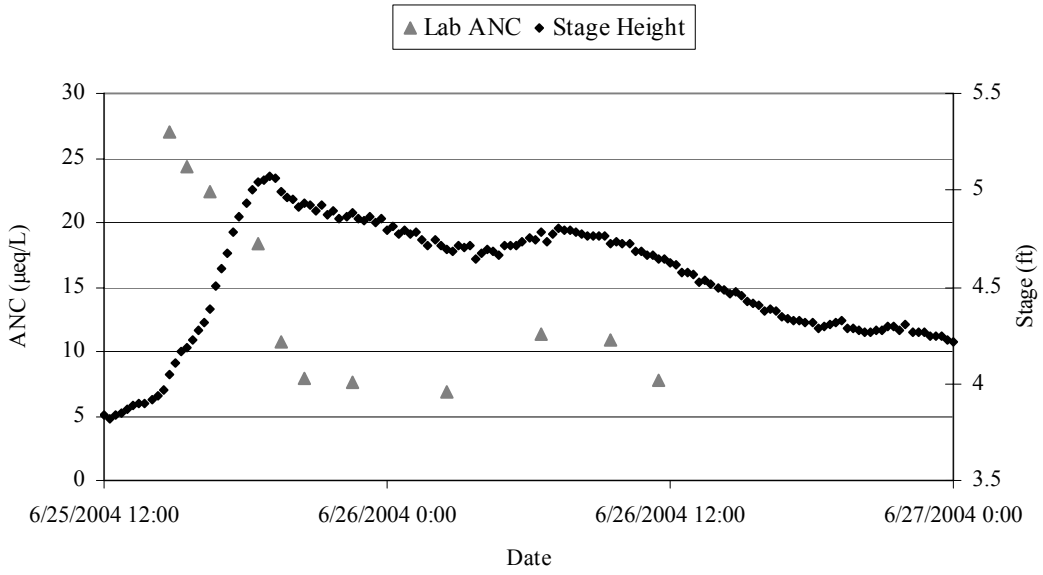

Figure 5-3. Storm event at Site 3 illustrating depressed ANC.

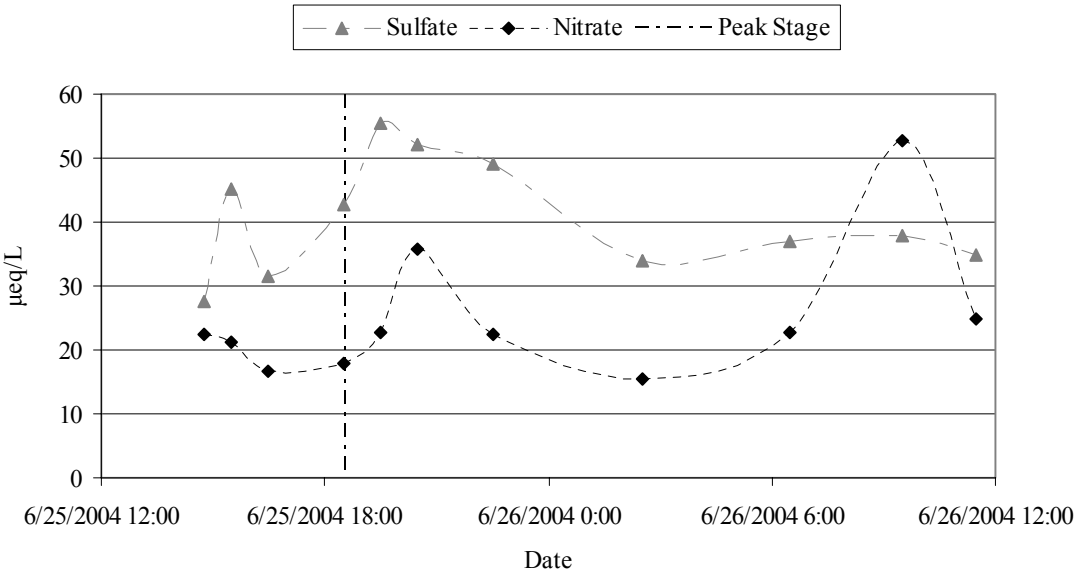

Figure 5-4. Storm event at Site 3 illustrating sulfate and nitrate fluctuations.

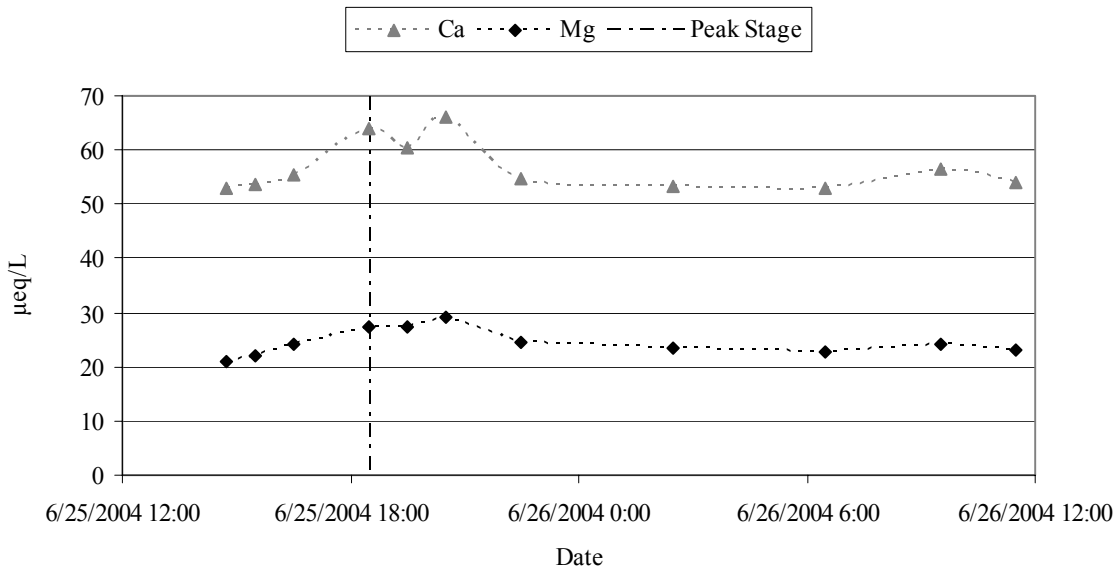

Figure 5-5. Storm event at Site 3 illustrating calcium and magnesium fluctuations.

The EPA freshwater criteria for aluminum are CMC (Criterion Maximum Concentration) = 750 μg/L and CCC (Criterion Continuous Concentration) = 87 μg/L. Aluminum concentrations did not come close to the CMC but stayed above the CCC during the entire storm event (Figure 5-6). The criterion for iron is CCC = 1000 μg/L but there is no CMC criterion for iron. The iron concentration never reached the CCC during this storm event nor any other storm event investigated. The criteria for zinc and copper are based on hardness of the water. The mean hardness as represented by the sum of calcium and magnesium was 4.06 mg/L as $CaCO_3$. This gave a CMC of 9.257 μg/L 0.799 μg/L for zinc and copper respectively. Figure 5-7 shows that zinc fluctuated between 0 and 0.09 mg/L and exceeded the CMC several times. Copper fluctuated from 0.0007 to 0.011 mg/L and exceeded the CMC during the length of the storm (Figure 5-8). Thus, both aluminum and copper concentrations exceeded recommend levels for at least 20.75 hours, i.e., the duration of the sampling.

2.4 Sonde Turbidity Behavior

As expected, turbidity increased during this storm event. Median sonde turbidity for Site 3 was 5.60 NTU which was exceeded for about eight hours during this event (Figure 5-9). Other storm events produced higher stream turbidity.

2.5 Sonde Temperature and Conductivity Behavior

Temperature and conductivity both varied during this storm event. The increased conductivity (Figure 5-10) is attributed to increased ions from precipitation. The decrease in temperature could also be attributed to colder precipitation entering the stream (Figure 5-11). However, both could be due to diel variations. Diel cycles will be discussed further in Chapter 7.

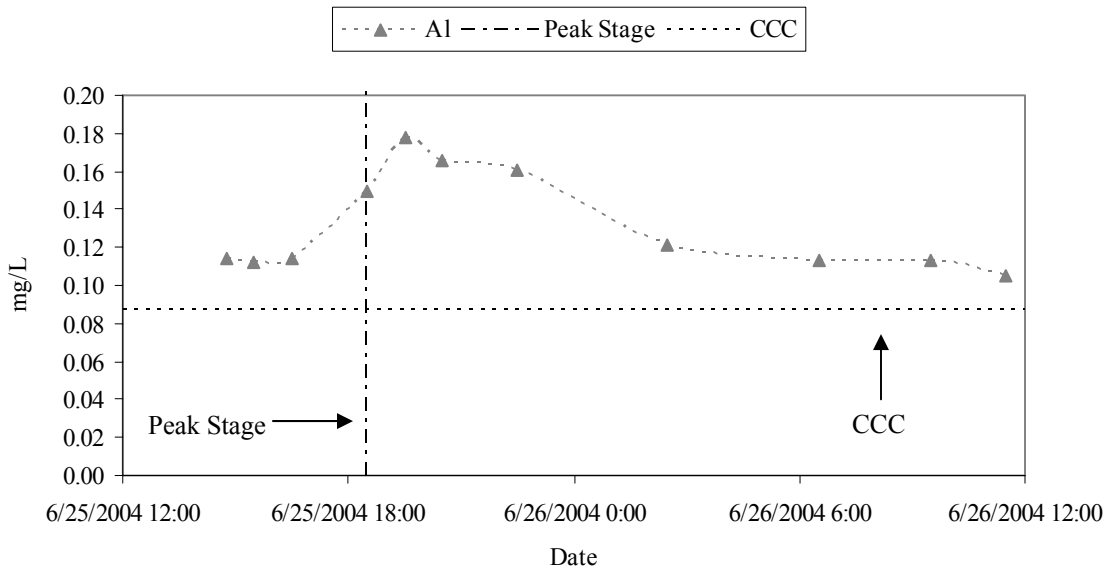

Figure 5-6. Storm event at Site 3 illustrating aluminum exceedence of CCC.

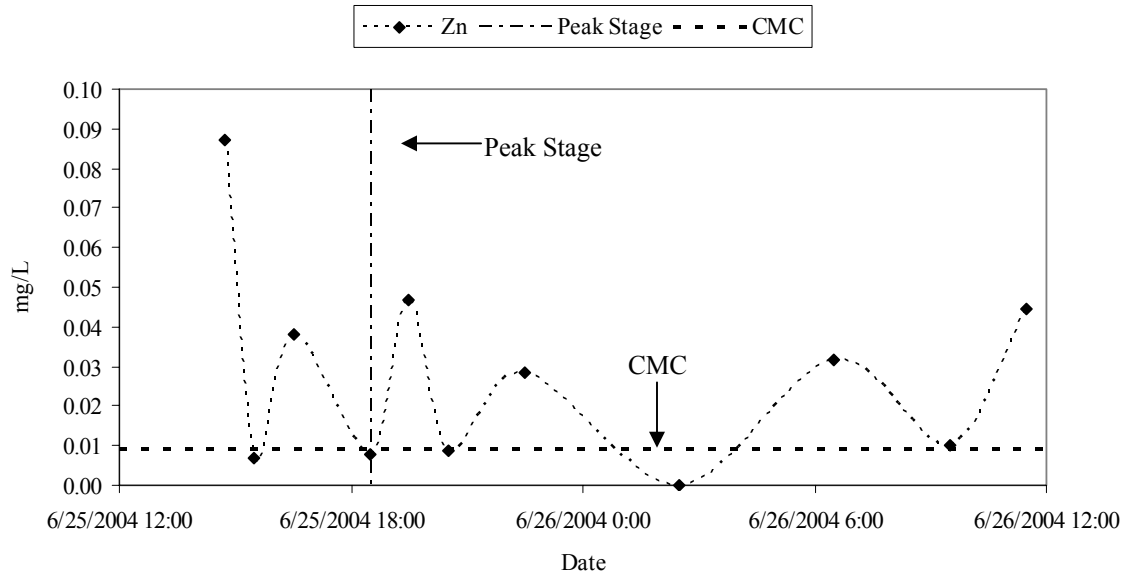

Figure 5-7. Storm event at Site 3 illustrating zinc exceedence of CMC.

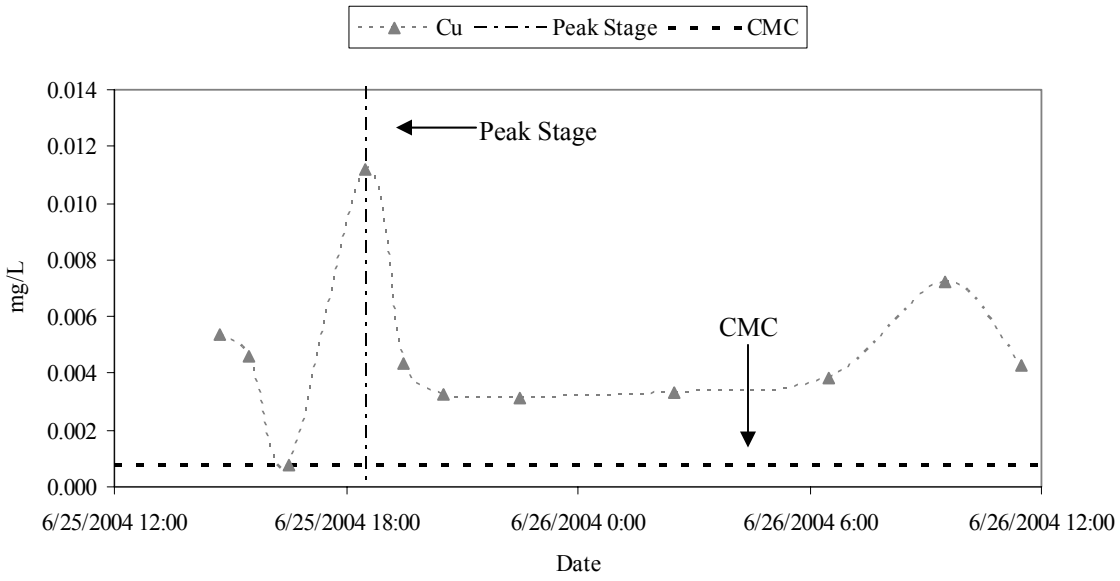

Figure 5-8. Storm event at Site 3 illustrating copper exceedence of CMC.

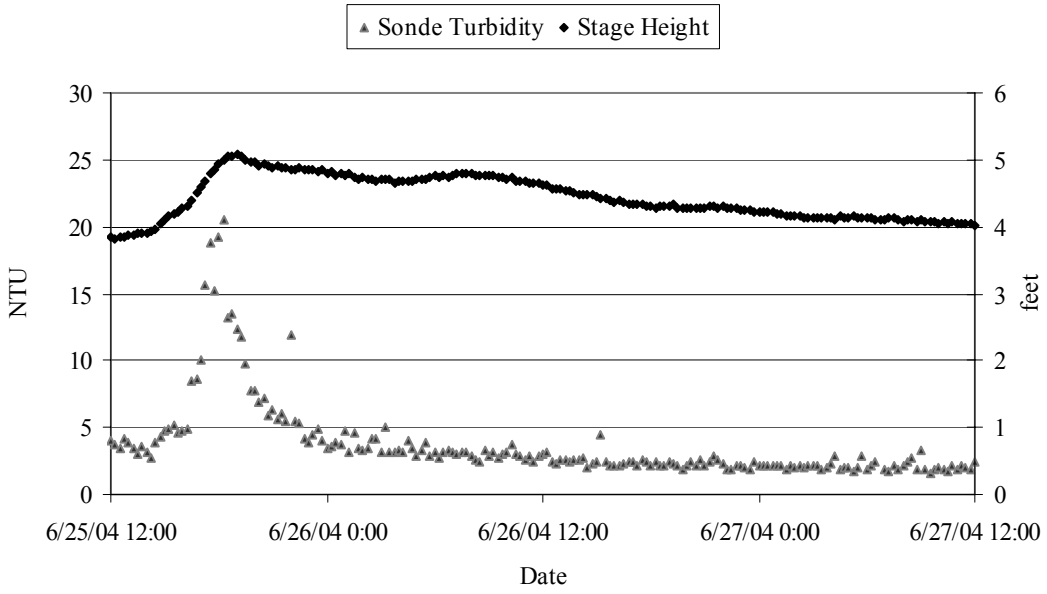

Figure 5-9. Turbidity vs. time at Site 3.

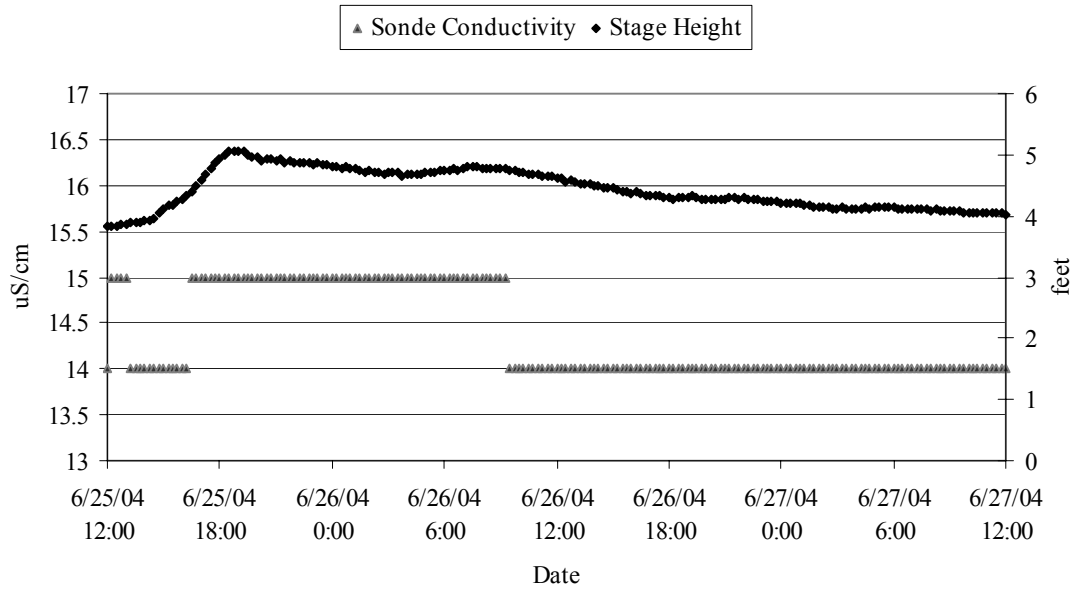

Figure 5-10. Conductivity vs. time for Site 3.

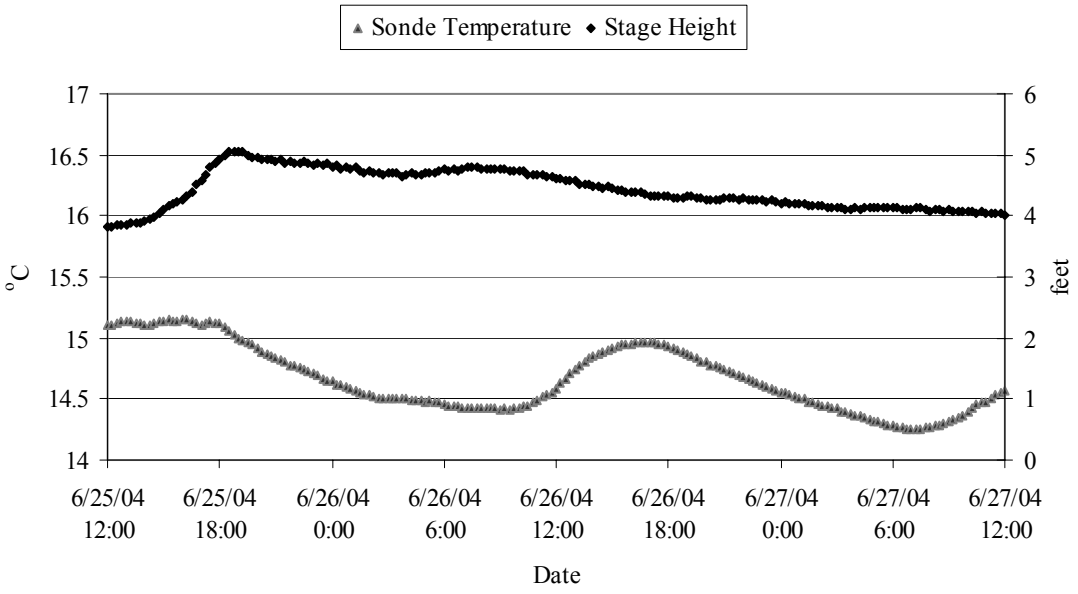

Figure 5-11. Temperature vs. time for Site 3.

3. Mass Balance of Precipitation Input Exported by Streams

Precipitation is believed to be the major cause of episodic acidification and increased ion input in the LPR watershed. If an ion were conservative, then the total equivalents brought in through precipitation should equal the total equivalents exported by the watershed. There are a number of considerations before making this assumption. First natural sources of sulfate or other ions must be considered. Second ion retention and exchange by the watershed must be considered. The delay in peak concentrations of ions discussed above raise questions about soil retention since the peak concentration should match peak precipitation input (peak stage). Also, part of the increased flow in streams may come from groundwater sources through a "piston effect." With these considerations in mind, the total ions brought into the watershed by precipitation should equal the total ions observed in stream storm flow. Once of the goals of this exercise was to see how close the mass balances would agree despite limited data and to understand what will be necessary to obtain better estimates.

3.1 Method

The first step was to estimate flow in order to obtain storm volume. There are a number of methods to estimate flow but due to limited resources, using Manning's equation to develop a rating curve was most practical. Site 2 was chosen since base flow and stream cross section data was available from the National Park Service Fisheries Biologist. Their data also gave a one point stage and flow calibration. The rating curve was developed using Haestad Methods FlowMaster®. FlowMaster® allows the user to chose from a variety of cross sectional areas, vary slopes and Manning's n, and output several graphs and tables. A trapezoidal shape was selected to represent the stream cross-

section with a Manning's n of 0.05. A Manning's n of 0.05 corresponds to a stony, natural stream. Data used in FlowMaster® for Site 2 is shown in Figure 5-12. The developed rating curve is shown in Equation 5-1.

$$\text{Flow} = 6.715*\text{Stage}^2 + 70.475*\text{Stage} \qquad \text{Equation 5-1}$$

Where:

Flow = stream flow at Site 2, cfs
Stage = depth measurement from sonde, ft

From Equation 5-1, a hydrograph was constructed from when stage began to increase from base flow to when stage decreased back to base flow. The area under the hydrograph represents total volume of water in cubic feet (Figure 5-13). Trapezoidal numerical integration was used to estimate this area as shown in Equation 5-2.

$$\text{Total Stream Volume} = \int_0^{tr} Q_{tr}\, dt = \Sigma \frac{Q_t + Q_{t-1}}{2} \Delta t \qquad \text{Equation 5-2}$$

Where:

Q_{tr} = flow at end of storm event
Q_t = flow at time t

The base flow was also estimated using numerical integration:

$$\text{Base Volume} = \frac{Q_0 + Q_{tr}}{2} \Delta t \qquad \text{Equation 5-3}$$

Where:

Q_0 = base flow prior to start of event

Subtracting base flow from total flow resulted in total storm volume.

$$\text{Storm Volume} = \text{Total Stream Volume} - \text{Base Volume} \qquad \text{Equation 5-4}$$

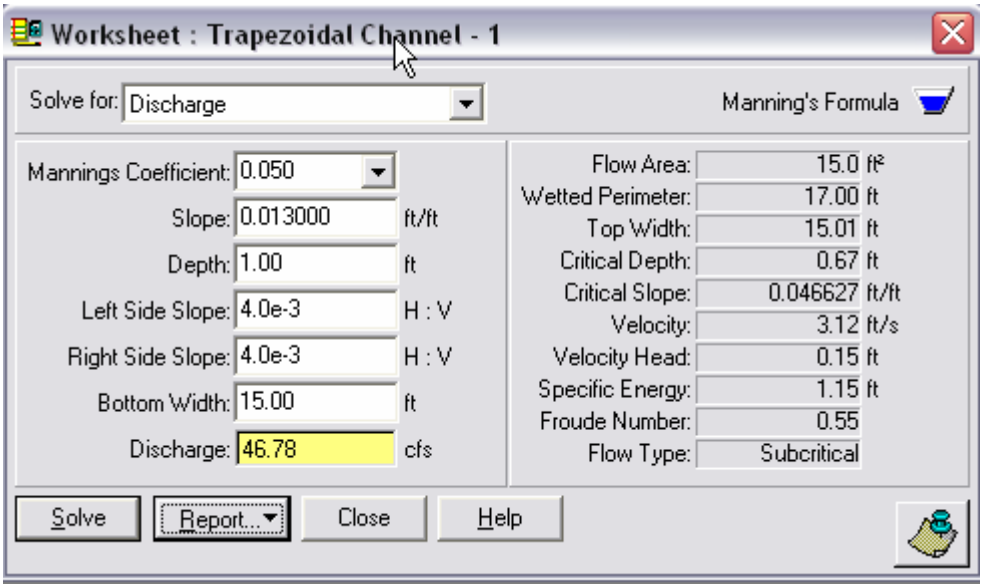

Figure 5-12. Data used to develop rating curve for Site 2 using Flow Master.

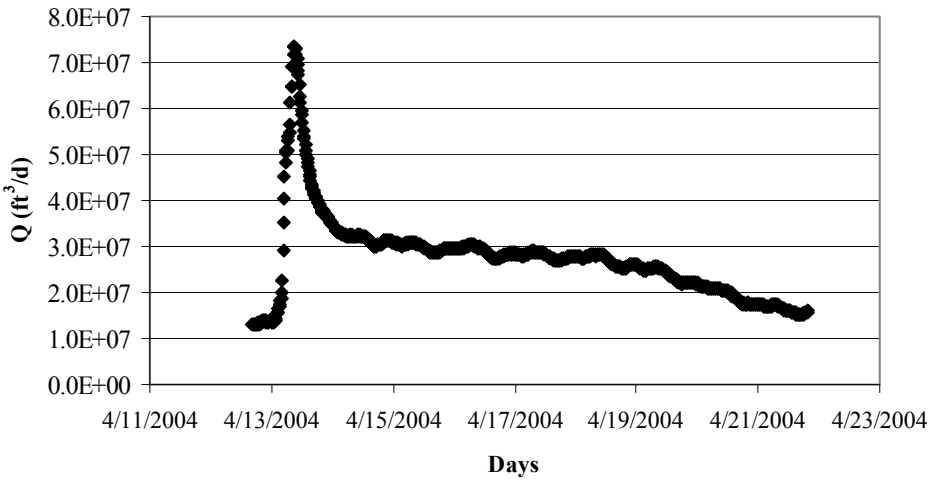

Figure 5-13. Estimated flow at Site 2 using Manning's Equation.

The next step was to estimate the quantity of precipitation that fell on the watershed. Two tipping bucket rain gauges located at Site 5 and 6 were used to estimate rainfall over the watershed. The NRCS Curve Number Method was used to estimate the quantity of precipitation that resulted in run-off. The dominate soil type is silt loam which corresponds to Type C SCS Hydrologic Soil Grouping (Wanielista et al 1997). The curve number selected was 70 which correspond to woods in good hydrologic condition (Wanielista et al. 1997). Assuming uniform rainfall the total volume of precipitation would be the watershed area multiplied by the total precipitation that resulted in run-off. The area of the LPR watershed is 30,636.59 acres. The total precipitation run-off and storm volume should be approximately equal.

The third step was to estimate the total load of ions in base and storm flow and precipitation. The concentration of ions in the stream were multiplied by the flow in liters per day and plotted against time in days (Figure 5-14). Numerical integration of the curve gives total load in μeq (mg for aluminum).

$$\text{Total Stream Load} = \int_0^{tr} C_{tr} Q_{tr}\, dt \cong \Sigma \frac{C_t Q_t + C_{t-1} Q_{t-1}}{2} \Delta t \qquad \text{Equation 5-5}$$

Where:

C_{tr} = Concentration of ion at end of storm event
C_t = Concentration of ion at time t

$$\text{Base Load} = \frac{C_0 Q_0 + C_{tr} Q_{tr}}{2} \Delta t \qquad \text{Equation 5-6}$$

Where:

C_0 = Concentration of ion prior to start of event

Subtracting the total load from base flow load gives storm flow load.

$$\text{Storm Load} = \text{Total Stream Load} - \text{Base Load} \qquad \text{Equation 5-7}$$

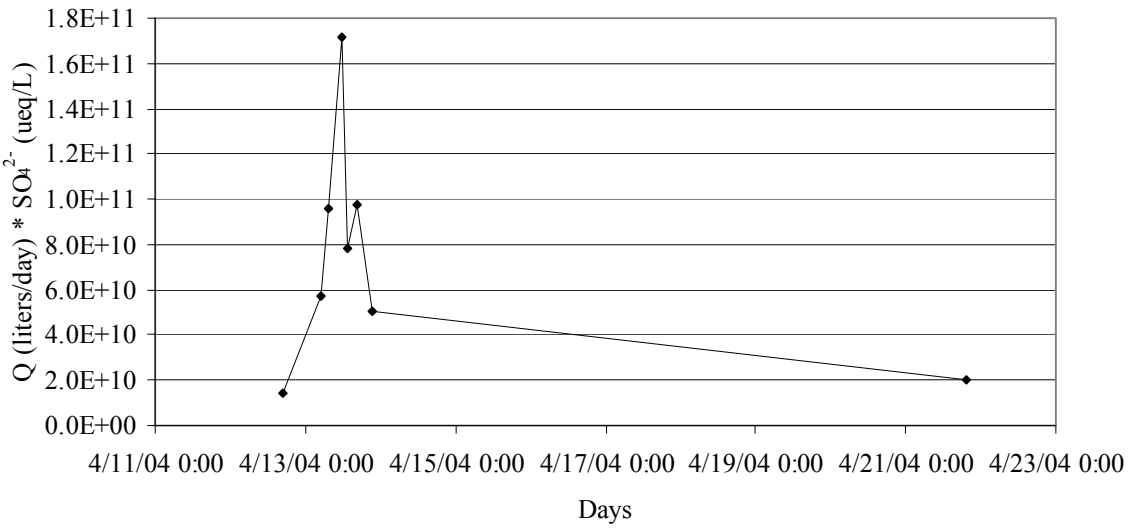

Figure 5-14. Estimated flow multiplied by sulfate concentration vs. days at Site 2.

Grab samples collected prior and after the storm event were used to estimate base flow loads. Storm event samples captured were used to estimate storm flow load.

Finally, estimation of load for precipitation was completed two ways: the bulk precipitation concentration of each ion multiplied by total run-off precipitation volume and by taking the mean of the sequential precipitation samples multiplied by the total volume of precipitation run-off.

3.2 Results and Discussion

Two storm events were analyzed using the technique described above. The first storm event began April 12, 2004 and decreased to base flow on April 21, 2004. Flow was estimated using Equation 5-1 through these dates and total volume was found to be 1.40E+08 ft^3. Base flow volume was estimated to be 7.61E+07 ft^3 resulting in 6.38E+07 ft^3 of storm flow volume. Tipping bucket rain gauges at Sites 5 and 6 both recorded 1.87 inches of precipitation from April 12, 2004 through April 21, 2004. Estimated precipitation run-off was 0.194 inches. This gave an estimated precipitation volume of 2.15E+07 ft^3. Storm flow volume and precipitation volume had a percent difference error of 66.3%. Independent calculations of storm volume and precipitation run-off volume were not close enough to make usable comparisons of ion loads. Instead precipitation run-off volume was assumed to equal storm run-off volume.

Load estimates are shown in Table 5-1 for the 4-12-04 storm event. Base flow loads increased from 1.63 to 147.76 times compared to storm flow. Notably, aluminum load increased 147.76 times from base to storm flow. Hydrogen concentrations increased 3.01 to 4.52 times when comparing stream base flow and storm flow. Sonde measurements resulted in smaller stream storm and base flow loads of hydrogen when compared to lab

Table 5-1. Estimated load results for Site 2 storm event on 4-12-04.

	Load				Ratios		
	Bulk Precipitation (BP)	Sequential Precipitation (SP)	Stream Storm Flow (SSF)	Stream Base flow (SBF)	SSF/SBF	SSF/SP	SSF/BP
Chloride (μeq)	3.30E+09	2.98E+10	3.53E+10	2.16E+10	1.63	1.18	10.69
Nitrate (μeq)	3.60E+10	8.51E+10	1.03E+11	4.06E+10	2.54	1.21	2.86
Sulfate (μeq)	5.12E+10	1.54E+11	1.29E+11	7.54E+10	1.71	0.84	2.52
Al (mg)	2.43E+07	2.51E+07	3.17E+08	2.16E+06	146.76	12.63	13.05
Lab $[H^+]$ (μeq)	7.77E+04	6.47E+04	3.94E+03	1.31E+03	3.01	0.06	0.05
Sonde $[H^+]$ (μeq)	--	--	2.04E+03	4.51E+02	4.52	0.03	0.03

measurements of grab and storm samples. However, sonde measurements showed a greater increase when comparing stream base and storm flow loads.

Ion loads in precipitation should match loads observed in storm flow loads if the ion is conservative and not retained by the water shed. Except hydrogen and aluminum, ratios for stream storm flow load compared to sequential precipitation loads ranged from 0.84 to 1.18. This indicates that the total mass in storm flow and precipitation are close. Ratios for bulk precipitation were higher and ranged from 2.52 to 10.69. This is likely an artifact of the differences in collection methods. Aluminum loads in storm flow were 12.63 to 13.05 times higher compared to sequential and bulk precipitation, respectively. It was expected that the aluminum load would be higher in stream loads since stream samples tend to have a higher concentration than precipitation samples indicating soil leaching sources caused from acid deposition mechanics. Storm loads showed significantly less hydrogen loads when compared to either precipitation loads. This indicates that the watershed is able to consume a large portion of the hydrogen loads brought in by precipitation.

The second storm event on 6-25-04 had an estimated stream base volume and storm of 1.83E+07 ft^3 and 5.63E+07 ft^3 respectively. Measured rainfall was 1.27 inches at Site 5 and 1.59 inches at Site 6. The mean was taken to represent uniform rainfall. Precipitation run-off was estimated to be 0.0675 inch. This resulted in 7.51E+06 ft^3 of total precipitation volume. The percent difference in volume estimates of precipitation and storm stream flow was 58.9% which was similar to the previous storm. Consistency in error indicates a valid approach to volume estimations but again precipitation run-off volume was assumed to be equal to stream storm volume.

Estimated load results are shown in Table 5-2. Chloride, sonde [H^+], and aluminum were the only ions that showed an increased load during stream storm flow compared to base flow. The previous storm event showed increases for all constituents. Precipitation flow loads ranged from 0.02 to 4.71 times storm loads. Aluminum loads when comparing storm and precipitation loads did not increase as much as the previous storm event. Stream base flow load of hydrogen did not increase as much as the previous storm during storm flow. Hydrogen loads increased 1.71 and 4.5 from base to storm flow for sonde hydrogen load for the 6-25-04 and 4-13-04 storm events, respectively. The differences between the results are likely due to the variation of storm event rain volume. The 4-13-04 storm event had a total of 1.35E+07 ft^3 more volume than the 6-25-04 storm event. Similarly, stage increased from 1 to 4.5 feet for the 4-13-04 storm event and from 2.5 to 4 feet for the 6-25-04 event. More volume obvious resulted in a greater increase in stage for the 4-13-04 event. Also, sonde data showed four distinct rises in stage from 6-21-04 to 6-24-04. The 6-25-04 storm event stage was higher at the onset of this storm event which likely means part of the base flow was actually storm flow from a previous event.

The estimates made are somewhat rough. To validate these findings better estimation of flow should be attempted perhaps by developing a rating curve based on actual flow data. Further time should be spent on applying the same method on different storm events to compare results. Precipitation chemistry is known to vary spatially and with time. The two precipitation sites did not show spatial variation but the sites are relatively close. Also, no though-fall precipitation samples were included. Future work should strive to include this missing information. This rough mass balance still provides

Table 5-2. Estimated load results for Site 2 storm event on 6-25-04.

	Load				Multiplicative Difference		
	Bulk Precipitation (BP)	Sequential Precipitation (SP)	Stream Storm Flow (SSF)	Stream Base flow (SBF)	SSF/SBF	SSF/SP	SSF/BP
Chloride (μeq)	4.55E+09	6.17E+09	2.15E+10	1.50E+10	1.43	3.48	4.71
Nitrate (μeq)	5.10E+09	2.20E+09	8.84E+09	3.48E+10	0.25	4.01	1.73
Sulfate (μeq)	2.03E+10	8.15E+09	6.96E+08	5.10E+10	0.01	0.09	0.03
Al (mg)	2.48E+07	2.53E+07	8.59E+07	6.49E+07	1.32	3.39	3.46
Lab [H+] (μeq)	2.84E+04	4.27E+03	5.81E+02	1.09E+03	0.53	0.14	0.02
Sonde [H^+] (μeq)	--	--	7.09E+02	4.13E+02	1.71	0.17	0.02

valuable information of the role precipitation has in the LPR watershed. The estimated loads do indicate a relationship between loads observed in precipitation and loads observed in storm volume.

4. Distribution of Ions during Storm Flow

This section will examine the distribution of ions during a storm event. The first flush phenomenon will be assessed to determine if a first flush exists in the LPR. The first flush has been defined various ways but is generally thought to carry the worst water quality. This is important since acute exposures of pollutants can be toxic to aquatic ecosystems. Also, knowing the distribution of ions helps to understand the complicated water quality dynamics.

4.1 Method

The general method for determination of volume of water and mass of ions may be seen in section 3.1. Dimensionless normalized mass for an ion is found by first determining the total mass during the storm event. Next, the cumulative mass is determined up to time t. Mass at time t is then divided by total mass to obtain a dimensionless ratio. It follows that the ratio would vary from 0 to 1 getting closer to one as the storm progresses until the time total storm flow mass has been reached. The dimensionless normalized volume is found in the same manner. Any units may be used as long as they are consistent. Equations 5-8 and 5-9 provide the means to assess ion distribution during a storm event:

$$N_m = m(t) / M \qquad \text{Equation 5-8}$$

$$N_v = v(t) / V \qquad \text{Equation 5-9}$$

Where:

N_m = Normalized mass ratio
N_v = Normalized volume ratio
m(t) = total ion mass up to time t
M = total storm flow mass
v(t) = total volume up to time t
V = total storm volume

The ratios up to time t are plotted on a scatter plot along with a Y = X line. Ratios above the line indicate mass accumulating in the stream faster than volume of water on average. Ratios on the line indicate an even distribution while ratios below indicate dilution on average. To assess individual time step accumulation or dilution the slope of two ratios are compared to a slope equal to one. If the slope is greater than one, accumulation of an ion is greater than accumulation of storm volume while a slope less than one indicates the opposite. A slope equal to one indicates an equal accumulation of an ion and storm volume.

4.2 Results and Discussion

Results for a storm event on 9-22-03 are illustrated in Figure 5-15. All ions start below the Y=X line, i.e. an initial dilution. Nitrate, sulfate, hydrogen, and aluminum then accumulate faster than water volume which is illustrated by being above the line. This gives evidence of a first flush for these ions. However, a first flush implies a very significant increase at the onset of a storm event. Lee et al. (2002) defined the first flush as 50% of the mass in the first 25% of the volume. By this standard no ions exhibited a first flush. Base cations and copper are below the line indicating dilution. Base cation dilution is discussed further in Section 5 of this chapter.

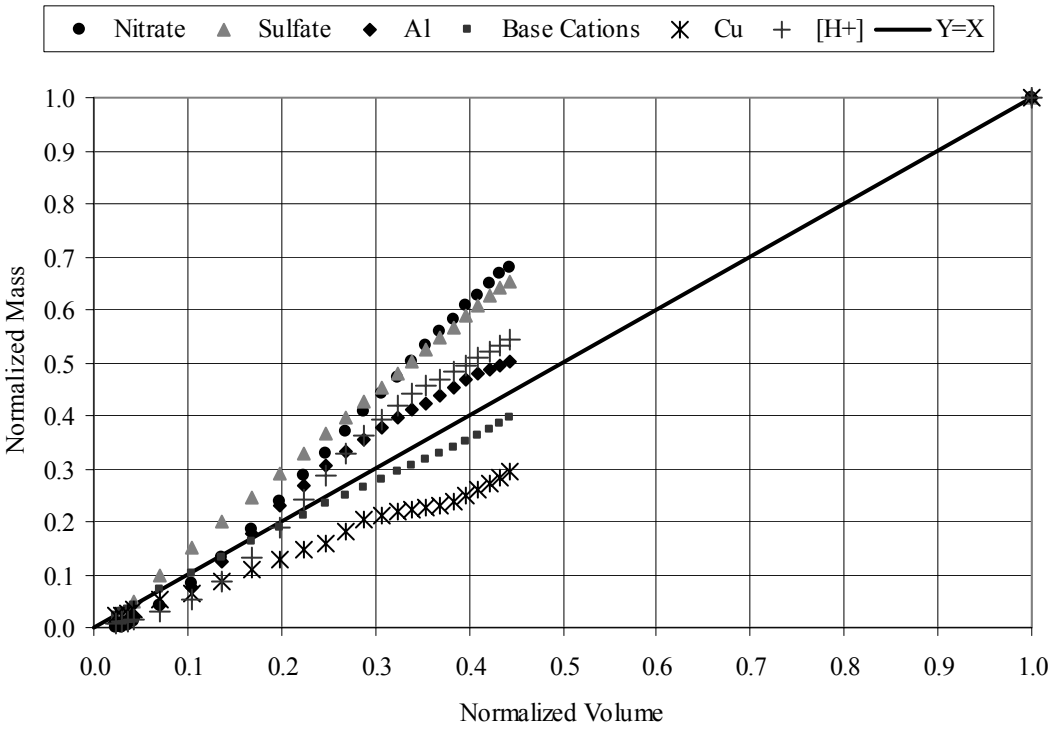

Figure 5-15. Ion distribution for Site 3 storm event on 9-22-03.

A complete analysis of the entire storm event was not possible since samples were taken only at the onset of the storm through about 45% of the total volume. The last sample represents a grab sample taken at the time flow reduced to base flow but the last sample of course gives a ratio of one. This leaves a large data gap to which the distribution of ions is unknown. This distribution estimation is likely good for sulfate and nitrate since almost 70% of their mass had accumulated by time the sampling ceased. Copper only had 30% of it total mass accumulated. It is unlikely that it would begin to increase faster than storm volume but this is uncertain without further investigation. Another storm event on 4-12-04 exhibited very similar behavior to this storm event except aluminum showed dilution.

Sonde hydrogen concentration was known throughout this storm event. It showed a dilution at the onset of the storm which was expected since pH often exhibited an initial upward pH spike (Figure 5-16). The ratios then show a very fast accumulation of hydrogen ions. Using 50% mass by the first 25% of volume, hydrogen did not exhibit a first flush. This is due to the initial decrease of hydrogen ions. Further investigation shows that once the ions began to accumulate faster than volume (where the ratios slope is greater than one) to the point that the slope of the curves begins to decrease, 25% of the total hydrogen mass accumulated while only 10% of the total volume accumulated. A rough translation of the mentioned standard is that double the mass must come faster than the volume. Using this criterion, hydrogen exhibited a delayed flush. The 4-12-04 storm exhibited similar behavior.

Turbidity, a surrogate for suspended solids, was also measure during the 9-22-03 storm event. Undergoing this analysis using turbidity NTU units resulted in unusual

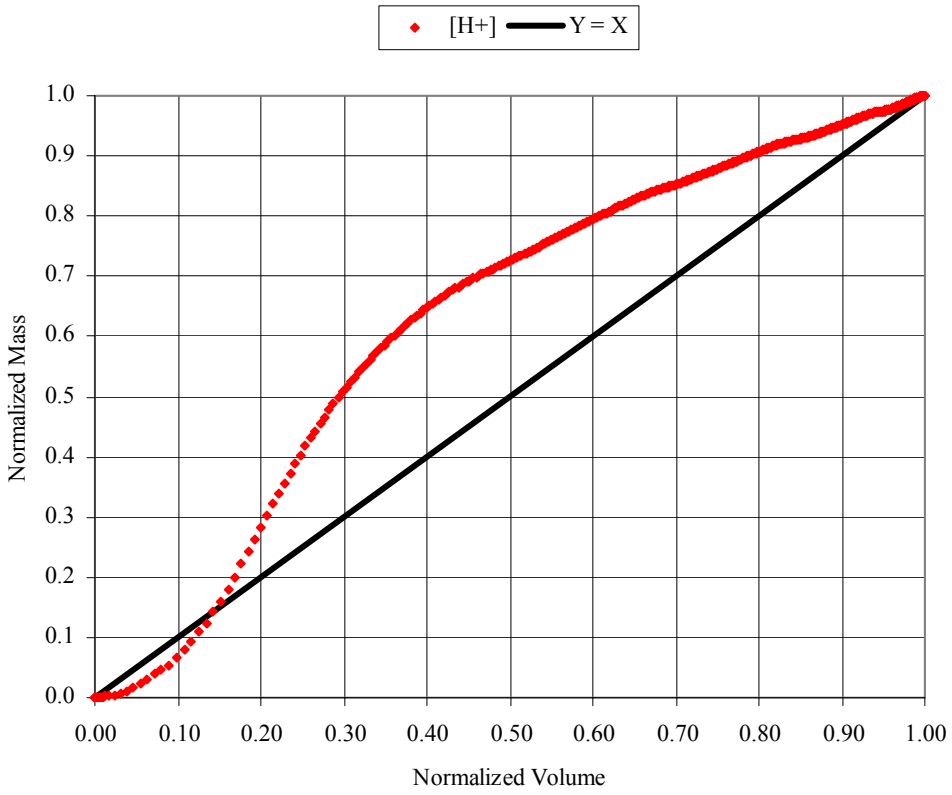

Figure 5-16. Sonde [H^+] distribution for Site 3 storm event on 9-22-03.

units. However, the final results is a dimensionless ratio that still provides information on how fast suspended solids are accumulating compared to storm volume. By the time 25% of storm volume had accumulated, over 60% of the turbidity had accumulated (Figure 5-17). This indicates a first flush for turbidity. This is important for a number of reasons. Suspended solids have been shown to cause adverse effects and knowing the behavior is important in assessing the health of a stream. Also, a first flush is now known to occur and the potential to worsen this phenomenon due to construction activities is possible.

5. Dominating Ions in Episodic Acidification

As discussed in Chapter 2, there are a number of factors involved in the mechanics of episodic acidification. Increased anions such as nitrate and sulfate have been identified as a major factor in ANC change. There are also studies that have shown base cation (calcium, magnesium, sodium, and potassium) dilution to be a major factor in episodic acidification (DeWalle and Swistock 1994). Organic acid input has also been shown to be important to a lesser degree. Increased aluminum concentrations though related to poor water quality has been shown to help offset depressed pH (DeWalle and Swistock 1994). This section will assess the dominate ions in the LPR watershed.

5.1 Method

Change in ANC can be used to assess which ions have the most affect. Rewriting an ion balance yields:

$$ANC = (Cb\ (Base\ Cations) + Al^{n+} + other\ cations) - (SO_4^{2-} + NO_3^- + Cl^- + other\ anions)$$

Equation 5-10

From Equation 5-10 it can be shown that decreased cations and increased anions

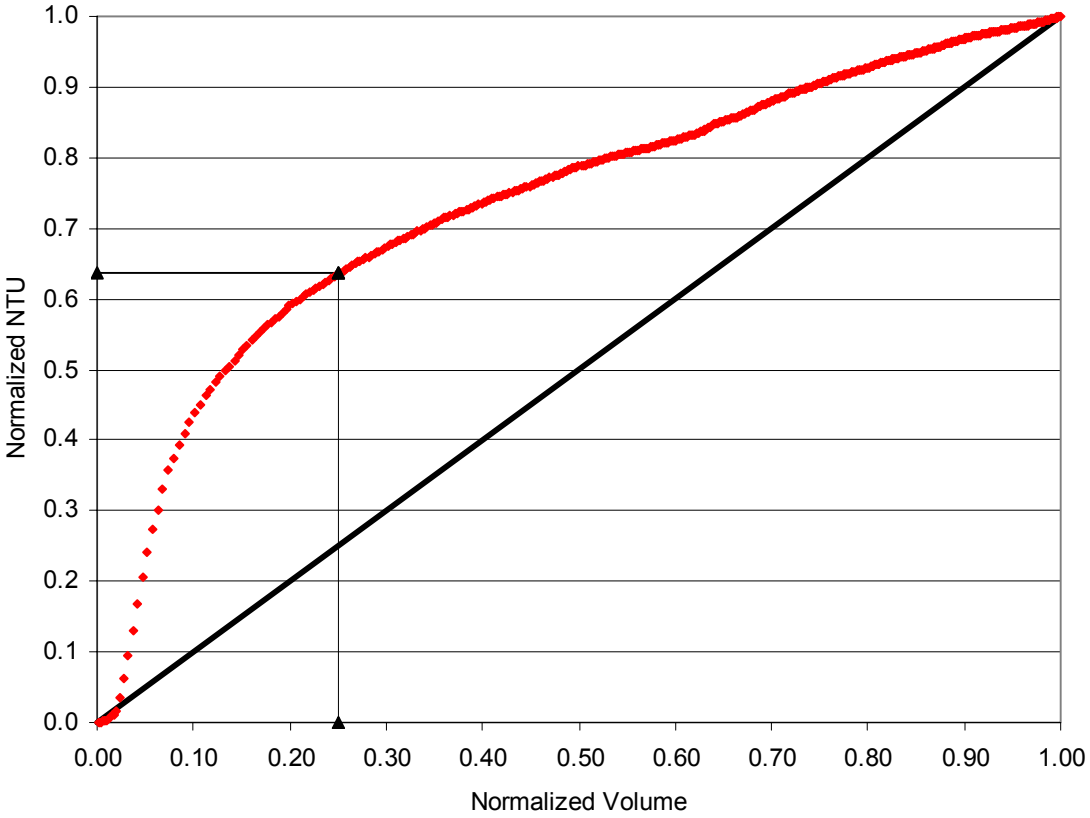

Figure 5-17. Sonde turbidity distribution for Site 3 storm event on 9-22-03.

corresponds to a decrease in ANC. The ion that has the greatest change from base flow concentration over the change in ANC has the most effect on ANC change. The more positive this ratio is the greater the effect on ANC changes. The ratios are calculated by:

$$\Delta ANC = (ANC_{base\ flow} - ANC_{storm\ flow}) \quad \text{Equation 5-11}$$

$$dCb = (Cb_{base\ flow} - Cb_{storm\ flow}) / \Delta ANC \quad \text{Equation 5-12}$$

$$dSO_4 = (SO_{4\ storm\ flow} - SO_{4\ base\ flow}) / \Delta ANC \quad \text{Equation 5-13}$$

$$dNO_3 = (NO_{3\ storm\ flow} - NO_{3\ base\ flow}) / \Delta ANC \quad \text{Equation 5-14}$$

$$dCl = (Cl_{storm\ flow} - Cl_{base\ flow}) / \Delta ANC \quad \text{Equation 5-15}$$

Changes in organic acid and aluminum were not considered though they may play an important role. Organic acid was not measured and aluminum speciation is unknown. The base flow chemistry is based on base flow samples collected every two weeks. The storm samples are taken by auto-samplers. A ratio as calculated by Equations 5-11 through 5-15 was calculated for all available storm samples. The ion with the highest ratio represents the dominating ion for that sample. The mean of the ratios was taken for each ion and represents the overall dominating factor of decreased ANC. Samples that had ANC changes less than five μeq/l were not used in calculating the mean due to their tendency to skew the mean. All available storm event samples from each site was used though not all storm samples could be included due to lack of good base flow representation prior to that event. In general base flow samples were taken within two weeks of collected storm samples. If no major precipitation event occurred between collection of base flow sample and storm samples, the base flow sample was considered representative of base flow conditions prior to that storm event.

5.2 Results and Discussion

As indicated by the mean ratio, sulfate was the dominating factor for each stream site (Table 5-3). At Site 2 sulfate only dominated 12.5% of the storm samples but still had the highest mean ratio. This indicates that even when it did not have the highest ratio it was still an important factor. All anions seemed to play a dominating role in ANC change. Past work has indicated clear dominance of at least one ion (DeWalle and Swistock 1994). Sulfate did have the highest mean ratio but the other anions had high number of samples that they dominated and had comparable mean ratios. Base cation dilution played the least significant role in ANC change but still could not be ignored. For the LPR, increased sulfate concentration is the dominating ion in ANC change. Although dilution of stream water with precipitation does account for some degree of depressed ANC, sulfate and nitrate ratios indicate acid deposition is the dominating cause of depressed stream ANC. Reduction of acid deposition would improve episodic ANC. However, depressed stream ANC would still be observed during storm events due to dilution.

Table 5-3. Mean dX Ratios for stream storm samples.

	Base cations		Sulfate		Nitrate		Chloride		N
Site	Mean d Cb	Samples Dominated	Mean d SO_4	Samples Dominated	Mean d NO_3	Samples Dominated	Mean d Cl	Samples Dominated	
Site 1	-0.26	37.9%	0.68	31.0%	0.51	20.7%	0.15	10.3%	29
Site 2	0.11	26.8%	0.39	12.5%	0.31	37.5%	0.24	17.9%	56
Site 3	0.10	22.9%	1.07	37.1%	0.55	11.4%	0.76	28.6%	35

6. Correlation Matrix of Site 2 Storm Flow Samples

Pearson r correlation matrixes of storm flow samples for Site 2 are shown in Table 5-4. Stage had a moderately negative correlation with pH. ANC and pH had a strong positive correlation as expected since changes in ANC generally involve consuming or increasing hydrogen ions. Conductivity, an indirect measurement of ions, was strongly correlated with calcium and magnesium indicating that they are dominating ions which is consistent with their divalent charge. Sulfate also had a moderate correlation with conductivity. ANC and pH had a moderate negative correlation with nitrate. This is expected since increased nitrate concentration is a symptom of acid deposition. The same trend was not observed with sulfate. Sulfate was found to be the dominate factor in ANC change so a low correlation with pH or ANC was not expected. Calcium and magnesium negative correlation with pH suggests leaching from soil sources since increased hydrogen ions from precipitation causes ion exchange with the soils. Calcium and magnesium had strong positive correlation with each other. Poor correlation with calcium and magnesium was observed with potassium and sodium. However, sodium and potassium had a strong positive correlation with each other.

7. Conclusions

The conclusions drawn from this chapter are:

- Increased stage resulted in depressed stream pH and ANC and an increase in nitrate, sulfate, aluminum, and other ions.
- Peak concentrations of ions often came after peak stage.
- Storm event beginning on 6-25-04 resulted in metal exceedances for aluminum, copper, and zinc for a duration of 20.75 hours.

Table 5-4. Pearson r correlation matrix for Site 2 storm flow samples (n = 60).

	Julian Date	Stage (ft)	pH	Conductivity (µS/cm)	ANC (µeq/l)	Cl (µeq/l)	NO_3 (µeq/l)	SO_4 (µeq/l)	Al (ppm)	Cu (ppm)	Zn (ppm)	Ca (µeq/l)	K (µeq/l)	Mg (µeq/l)	Na (µeq/l)
Julian Date	1	0.088	0.362	-0.722	0.076	0.166	0.077	-0.301	-0.245	-0.014	-0.214	-0.460	0.195	-0.376	0.325
Stage (ft)	0.088	1	-0.488	0.304	-0.214	-0.093	0.149	0.153	0.317	0.126	0.233	0.384	0.124	0.456	-0.133
pH	0.362	-0.488	1	-0.384	0.743	-0.053	-0.435	-0.230	-0.207	0.156	-0.307	-0.532	-0.087	-0.645	0.059
Conductivity (µS/cm)	-0.722	0.304	-0.384	1	0.063	-0.128	0.038	0.454	0.198	0.131	0.284	0.725	0.012	0.704	-0.223
ANC(µeq/l)	0.076	-0.214	0.743	0.063	1	-0.184	-0.512	-0.153	-0.230	0.211	-0.078	-0.046	-0.167	-0.349	-0.012
Cl (µeq/l)	0.166	-0.093	-0.053	-0.128	-0.184	1	0.293	0.168	-0.193	-0.216	-0.220	-0.075	0.750	0.152	0.773
NO_3 (µeq/l)	0.077	0.149	-0.435	0.038	-0.512	0.293	1	0.675	-0.066	-0.069	-0.036	0.128	0.263	0.366	0.190
SO_4 (µeq/l)	-0.301	0.153	-0.230	0.454	-0.153	0.168	0.675	1	0.022	0.148	-0.075	0.235	0.145	0.395	-0.140
Al (ppm)	-0.245	0.317	-0.207	0.198	-0.230	-0.193	-0.066	0.022	1	0.216	0.122	-0.059	-0.190	0.050	-0.332
Cu (ppm)	-0.014	0.126	0.156	0.131	0.211	-0.216	-0.069	0.148	0.216	1	0.212	-0.021	0.029	-0.256	-0.275
Zn (ppm)	-0.214	0.233	-0.307	0.284	-0.078	-0.220	-0.036	-0.075	0.122	0.212	1	0.322	-0.010	0.246	-0.131
Ca (µeq/l)	-0.460	0.384	-0.532	0.725	-0.046	-0.075	0.128	0.235	-0.059	-0.021	0.322	1	0.042	0.769	0.000
K (µeq/l)	0.195	0.124	-0.087	0.012	-0.167	0.750	0.263	0.145	-0.190	0.029	-0.010	0.042	1	0.231	0.668
Mg (µeq/l)	-0.376	0.456	-0.645	0.704	-0.349	0.152	0.366	0.395	0.050	-0.256	0.246	0.769	0.231	1	0.110
Na (µeq/l)	0.325	-0.133	0.059	-0.223	-0.012	0.773	0.190	-0.140	-0.332	-0.275	-0.131	0.000	0.668	0.110	1

- Mass balances indicated some differences between precipitation loads and stream storm loads of ions but a relationship is indicated.
- Mass balances show large difference in aluminum loads between stream storm and precipitation loads for storm event on 4-12-04. This indicates soil sources of aluminum contribute to storm stream loads.
- A first flush is not indicated using the normalized volume and mass method for sulfate, nitrate, base cations, and hydrogen ions. However, these ions accumulated faster than storm volume indicating a build up of these ions. This is consistent with acid deposition mechanics.
- Sonde hydrogen concentrations did not indicate a first flush but a delayed flush was observed.
- Turbidity was shown to have a first flush.
- Sulfate dominated ANC change during storm events. This is consistent with acid deposition mechanics. Decreased acid deposition would improve episodic acidification.

Chapter VI. Multiple Linear Regression of Sonde Data

1. Introduction

Episodic acidification is a common problem in the GRSM and the ability to model it can be a valuable tool for understanding its causes. It is important to note that causation cannot be established from a regression model in an observational study. Only association between the predictor and response variables can be established (Dunlop and Tamhane 2000). Nevertheless, cause may be implied through the associations found.

Two variables from the sonde data were selected for model development based on their importance to water quality and aquatic life: pH and turbidity. Multiple linear regression will be used to construct significant models for pH and turbidity. The models will only include explanatory variables that actually represent controlling water quality forces. Variables that simply improve fit will not be included. Regression diagnostics will ensure development of the best possible models. The developed model can then be applied to future data to assess any changes. If the model does not describe water quality during construction and post construction it can be inferred that construction activities or changes in watershed dynamics has altered water quality.

Five to eight storm events were selected depending on the site to comprise a model building and validation data set. The total number of storm events exceeded twenty-five which precluded including all storm events. Storm event selection was designed to include a representative set of storm events (e.g. varying increases in stage and length of storm). In some cases, different storm events had to be used for each site due to equipment failures. For the purpose of model building, the beginning of a storm

event is defined as an increase of 0.5 feet in stage. The end of the storm event is designated when the stage decreases to the point at which the storm event began. All storm events, when possible, were confirmed by rain gauges located in the watershed.

2. Explanatory Variables

There are a number of variables that will be considered for inclusion in the pH and turbidity linear regression models. Variables will be considered in two parts: data collected directly from the sonde and other possible variables.

2.1 Sonde Data

The first step in the development of the pH and turbidity storm event models was to construct a Pearson correlation matrix of storm event sonde data (Table 6-1). This served two purposes: to assess associations with pH and turbidity and to identify any potential multi-collinearity problems. The Pearson r value in Table 6-1 shows that a strong negative correlation exists between pH and stage. All sites have a Pearson r above -0.70 for pH and stage. Turbidity has a slight correlation with stage, however, increases in stage increases the velocity of the stream, which causes sand, rocks, and other debris to become mobile. This suggests that a relationship between stage and turbidity must exist. Turbidity and stage at Site 2 had a Spearman's Rho value of 0.7571 (p=0.0000) indicating that a non-linear relationship may exist. Stage will be considered for inclusion in the pH and turbidity model.

Changes in cations and anions play a role in pH changes. Conductivity is an indirect measurement of ions and should be related to pH changes. Site 1 and 3 had slight negative linear correlation between conductivity and pH. Conductivity will be further investigated as a possible explanatory variable. Conductivity and stage had a

Table 6-1. Pearson r correlation matrix for selected storm events at Sites 1 – 4.

Parameter	Julian Day	Temperature (°C)	Conductivity (µS/cm)	Stage (ft)	pH	Turbidity (NTU)
Site 1						
Julian Day	1.0000	0.8767	0.3695	0.2014	-0.0154	0.0050
Temperature (°C)	0.8767	1.0000	0.3538	0.1525	0.0352	0.0420
Conductivity (µS/cm)	0.3695	0.3538	1.0000	0.5056	-0.3408	0.1576
Stage	0.2014	0.1525	0.5056	1.0000	-0.7281	0.2578
pH	-0.0154	0.0352	-0.3408	-0.7281	1.0000	-0.1217
Turbidity (NTU)	0.0050	0.0420	0.1576	0.2578	-0.1217	1.0000
Site 2						
Julian Day	1.0000	0.8808	-0.2299	0.2946	-0.0163	0.1005
Temperature (°C)	0.8808	1.0000	-0.0472	0.2606	0.0370	0.1285
Conductivity (µS/cm)	-0.2299	-0.0472	1.0000	0.1551	-0.0913	0.1370
Stage (ft)	0.2946	0.2606	0.1551	1.0000	-0.7825	0.3022
pH	-0.0163	0.0370	-0.0913	-0.7825	1.0000	-0.1073
Turbidity (NTU)	0.1005	0.1285	0.1370	0.3022	-0.1073	1.0000
Site 3						
Julian Day	1.0000	0.7830	0.3770	0.3951	-0.2211	0.1814
Temperature	0.7830	1.0000	0.1638	0.3719	-0.1223	0.2120
Conductivity (µS/cm)	0.3770	0.1638	1.0000	0.1426	-0.2467	0.1662
Stage	0.3951	0.3719	0.1426	1.0000	-0.7960	0.3900
pH	-0.2211	-0.1223	-0.2467	-0.7960	1.0000	-0.2051
Turbidity (NTU)	0.1814	0.2120	0.1662	0.3900	-0.2051	1.0000
Site 4						
Julian Day	1.0000	-0.7659	-0.0737	-0.3983	0.1690	No turbidity probe.
Temperature	-0.7659	1.0000	0.5037	0.2151	0.0774	
Conductivity (µS/cm)	-0.0737	0.5037	1.0000	0.1603	0.0572	
Stage	-0.3983	0.2151	0.1603	1.0000	-0.7354	
pH	0.1690	0.0774	0.0572	-0.7354	1.0000	

.

Pearson r-value of 0.5 signifying a multi-collinear problem may exist if both were included as independent variables in a regression model.

2.2 Other Explanatory Variables

This section will be a brief overview of other explanatory variables considered. Neither pH nor turbidity had a strong linear relationship with Julian day. Transformations of Julian day into sine and cosine functions have been used in past models with success to reflect seasonality. Additionally, the following variables will be considered as explanatory variables:

- Length of the preceding antecedent period
- Rain volume and intensity
- Rate at which peak stage is reached
- Rate of change in stage between each sonde reading

3. Model Building Techniques and Diagnostic Procedures

A variety of techniques and diagnostic can be employed to develop multiple linear regression models. This section will outline the procedures used to build the pH and turbidity multiple linear regression models using the selected possible variables from Section 2.

3.1 Assessing Linearity

The first step in model building was to plot the dependent variable versus all the independent variables. This serves several purposes. It gives a visual assessment of linearity and may indicate a transformation of the dependent or independent variable was necessary. It also allowed the first variable to be selected for inclusion in a multiple linear regression model based on simple linear regression r^2 values.

3.2 Hypothesis Testing

Linear regression is often referred to as a parametric procedure but this is only true when referring to the associated hypothesis testing since residuals are required to be normally distributed. One important hypothesis test was to determine if regression coefficients are significantly different from zero. If a coefficients p-value was not large enough then the variable was not significant and its inclusion in the model was not warranted. Variables will only be included if they are significant at a 95% confidence level. A second important hypothesis test was analysis of variance approach. This test gives information of whether a statistically significant amount of variance has been explained by the included explanatory variables. A model was only accepted if it explains a significant amount of variance at a 95% confidence level.

3.3 Coefficient of Determination

The coefficient of determination (r^2) is a similar measurement to analysis of variance in that it measures the fraction of variance explained by the model. It is the ratio of model sum of squares divided by the total sum of squares. It follows that reducing the error in the model causes the ratio to move closer to one or 100% of variance in y explained by the model. There is no set standard of how high r^2 should be for a regression model but is subjective to its application.

3.4 Multi-Collinearity

Multi-collinearity can cause serious problems in multiple linear regression models and occurs when one or more variables are closely related to another variable. There are several problems associated with multi-collinearity, which include regression coefficients having unrealistic magnitude and sign. One diagnostic tool to assess multi-collinearity is

the variance inflation factor (VIF). VIF values over ten indicate serious multi-collinearity with ideal VIF values being equal to one. Multi-collinearity is almost certain to occur when one variable is a function of another such as x^2. The most common solution is to center the function with the mean of the data. Variables that are not a function of each other that have a high VIF value should be excluded from the model.

3.5 Residual Analysis

Residuals should be evaluated for normality as discussed in Section 3.2. Additionally, residuals were plotted versus predicted values to visually inspect for curvature and heteroscedasticity. Also a plot of residuals versus time and all explanatory variables were constructed. All plots should appear random with no patterns. If patterns exist residuals may be serially correlated. This can result in less than optimal regression estimations and can cause confidence intervals to be too narrow (Helsel and Hirsch 1992). Serial correlation can be assessed by the plots described above or by formal tests such as the Durbin-Watson statistic. However this test is not possible with this data set since it requires evenly spaced time intervals. Another test is to lag the residuals then measure the correlation between residuals and lag residuals. High correlation values indicate serial correlation.

3.6 Validation Data Set

An authoritative method to assess a model's predictive power is to apply it to a validation data set. The validation data set should be a random and representative sample of the data. The amount of variance explained by the model for the validation data set is then assessed. The validation data set may also be used to assess explanatory variables. Once the original model has been applied to the validation data set, explanatory variables

can then be dropped then reapplied to the validation data set to determine if fit is improved. Improvement fit indicates the dropped explanatory variables may be excluded from the original model.

3.7 Outlier and Leverage Points Analysis

There are a number of tools to evaluate outliers and leverage points. The hat matrix ("hats") was used to assess leverage points in the x direction. Studentized residuals were used to assess outliers in the y direction. Cook's D was used for points may be outliers and have high leverage. The Press statistic was also used to evaluate the predictive ability of the model. The Press statistic omits one observation at a time then fits the model and measures the deviation from the actual and predicted dependent variable. This step was repeated while dropping one explanatory variable at a time. The model with the lowest Press statistic is considered the best model.

4. Multiple Linear Regressions for Storm Event pH Prediction

Stage had the strongest correlation with pH and will be considered first. A simple linear regression of pH vs. stage is shown in Figure 6-1. The resulting model had a r^2 value of 0.63. There are a number of patterns present in the plot. Some of the patterns can be traced back to individual storm events. As discussed in Chapter 5, the minimum pH tends to occur after the peak stage. In order for a linear relationship to be developed these two extremes should coincide. A linear regression model was developed to determine the time that stage should be lagged for peak stage and minimum pH to coincide. Several variables were investigated to predict the time between the minimum pH and maximum stage including days preceding with no precipitation, average rain intensity over the course of the storm event, total rise in stage, total time taken to reach

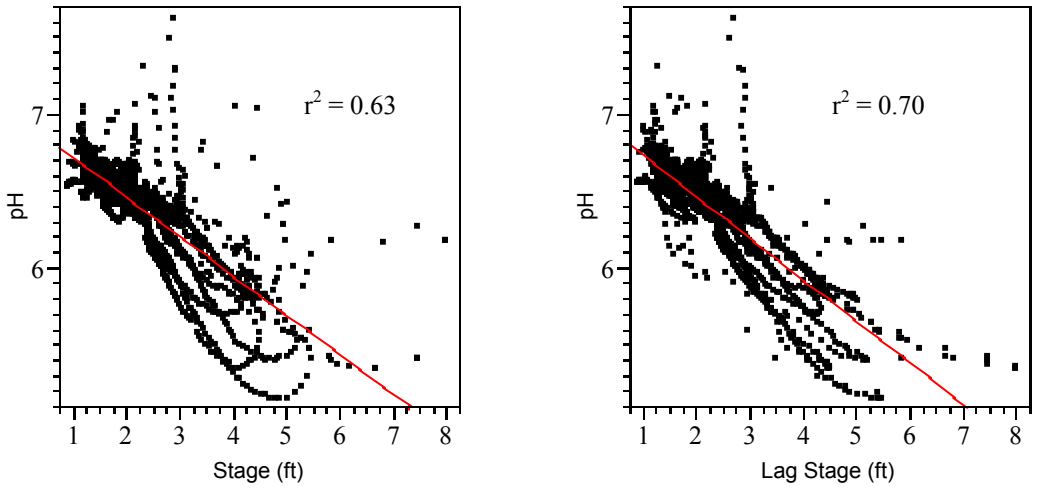

Figure 6-1. pH vs. stage (left) and pH vs. lag stage (right) at Site 2.

maximum stage, and maximum stage intensity. Maximum stage intensity (feet/hr) was chosen as the best predictor based on coefficient of determination values (r^2) and model p-values. Maximum stage intensity was found by dividing the difference in maximum stage and stage at the onset of the storm event by the time elapsed. Maximum stage intensity at Sites 1 – 3 explained enough variance to be significant at a 95% confidence level. Site 4 had similar pH lags but no variable investigated was able to predict this lag. The stage lag equation below was used to determine what lag interval the stage would have in the model and validation data sets.

$$\text{pH Lag} = b_o - b_1 * \text{Maximum stage intensity} \qquad \text{Equation 6-1}$$

Where:

pH Lag = stream pH recorded by sonde with predicted lag time, minutes
b_i = regression coefficient
Rate to maximum stage = Δ in stage between maximum stage and initial stage divided by Δ in time, ft/day

The coefficients for Equation 6-1 are shown in Table 6-2 along with their respective r^2 values. Equation 6-1 was used to predict appropriate lag in stage for each storm event in the model building data set. A simple linear regression was then completed with stage replaced with lagged stage. After replacing stage for lagged stage predicted by Equation 6-1, the r^2 value increased for the simple linear regression model from 0.63 to 0.70 at Site 2 (Figure 6-1). Sites 1 and 3 had similar increases.

The total precipitation volume in inches during each storm was used as an explanatory variable. Total rain volume proved to be significant at a 95% confidence level for all sites and for Site 2 raised the r^2 value from 0.70 to 0.75 with similar increases at Sites 1 and 3. This variable was not used for the development of the Site 4 model since a considerable amount of data was collected prior to the installation of rain gauges.

Discussed in Chapter 7, a pH diel cycle occurs at each of the four stream sites. This type of cycle is often modeled with sine and cosine functions. The sine and cosine of θ (where θ is equal to the day fraction multiplied by 2π) were added as possible variables to describe the diel cycle. For Site 2, adding sine and cosine increases the r^2 value from 0.750 to 0.759. Sites 1 and 3 had similar small increases in r^2. This may seem like an insignificant increase but it results in the predicted pH following a similar oscillating cycle seen in the actual pH. For Site 3, the sine function was not a significant variable at a 95% confidence level. Helsel and Hirsch (1992) recommended always adding both sine and cosine functions because it forces the phase shift to be determined by the data. The developed pH model is shown in Equation 6-2 and the model parameters are shown in Table 6-3.

Table 6-2. Model coefficients to predict lag period between stage and pH.

Site Name	Regression Coefficient		r^2	N
	b_o	b_1		
Site 1	192.41	3.86	0.80	5
Site 2	156.71	3.63	0.66	8
Site 3	157.83	3.27	0.47	5

Table 6-3. Models parameters for storm event pH model.

Site Name	Regression Coefficient					Model p	r^2	N
	b_o	b_1	b_2	b_3	b_4			
Site 1	7.045	0.395	0.053	-0.023	-0.046	0.0000	0.630	3065
Site 2	6.897	0.283	0.073	-0.023	-0.029	0.0000	0.759	3466
Site 3	7.384	0.422	0.057	0.005	-0.018	0.0000	0.723	2823
Site 4	6.744	0.981	--	0.014	- 0.004	0.0000	0.541	3558

$$pH = b_0 - b_1*\text{Lagged Stage} + b_2*\text{Rain Volume} + b_3*\sin(\theta) + b_4*\cos(\theta)$$

Equation 6-2

Where:

pH = stream pH recorded by the sonde
b_i = regression coefficient
Lagged Stage =Stage shifted forward according to Equation 6-1, ft
Rain Volume = total rain volume during the storm, inches
θ = day fraction multiplied by 2π

4.1 Multiple Linear Regression Diagnostics Results

The variables listed in Section 2.1 and 2.2 were only used if they were significant at a 95% confidence level. Conductivity was a significant explanatory variable at Sites 1 – 3 but was not included in the storm event pH model for three reasons. First, the r^2 improvement was minimal at all sites. Second, conductivity and pH are commonly measured simultaneously and to use one to predict the other does not make sense except in case of data loss. Third, the model's prediction variables should be causative variables such as precipitation volume and watershed characteristics. Conductivity, like pH, is a result of these causes rather than a cause in itself.

The amount of variance explained the by the models varied from 54.1% to 75.9% for the developed model depending on the site. The r^2 values were acceptable compared to past models developed from park data. The model p-values indicate that the amount of variance explained was significant at any reasonable confidence level.

Using Site 2 as an example, the normal quantile plot for residuals are shown in Figure 6-2. The residuals deviate significantly from a straight line indicating lack of normality. The large number of outlying residuals points causes the tails to exhibit extreme curvature. To further confirm this, a goodness of fit test was used. Normality was rejected at any reasonable confidence level ($p=0.0100$). The resulting confidence intervals for the parameter estimates are likely narrower than predicted.

Examination of residual plot in Figure 6-3 reveals that the residuals are not random and have a dependent pattern. The distinct patterns can be traced back to several common causes: the minimum pH and maximum stage do not align perfectly, the pH

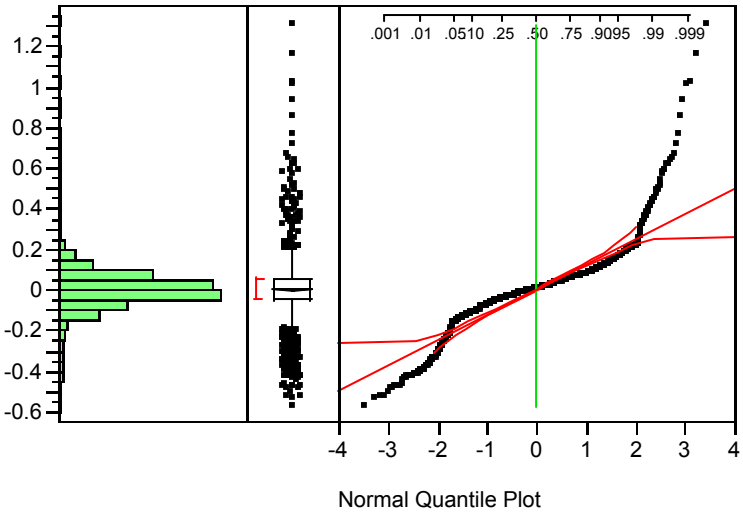

Figure 6-2. Determination of normality of residuals at Site 2 for pH storm model.

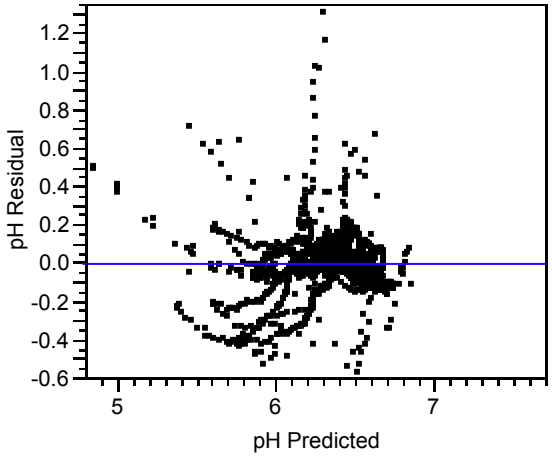

Figure 6-3. Residual plot from Site 2 pH storm model.

spikes seen at the beginning of storm events cannot be explained by any of the variables present, and the diel cycle is not modeled perfectly by the sine and cosine functions.

With high frequency data such as 15-minute sonde data, serial correlation is almost certain to occur. This can result in less than optimal regression estimations and can cause confidence intervals to be too narrow (Helsel and Hirsch 1992). Site 2 lagged residuals had a Spearman's Rho correlation value of 0.9780 indicating serial correlation. All sites had similar results. There are several methods are available to reduce serial correlation. For example, random subset sample data sets were selected with little success in reducing serial correlation. Other methods are beyond the scope of this document.

There were a number of outlying and leverage points that warranted investigation. Hats above 0.013 indicate a possible outlier in the x direction. A total of seven hats were above 0.013 for Site 2. These seven outliers were traced to one storm event in which the peak stage exceeded all other storm events by two feet. The seven points were not excluded. Sites 1 and 3 had similar results. Eighty-eight large studentized residuals were investigated for Site 2. The residuals tended to correspond with the minimum pH values and upward pH speaks generally seen at the onset of a storm event. No points could be excluded. Sites 1 and 3 had similar results. No Cook's D points indicated problems. No points could be excluded since they represent actual stream conditions.

The principle of parsimony states that the simplest model is usually the best. For example, the model was developed without rain volume and applied to the validation model set. A better fit was obtained with the rain volume variable included, which

indicates that inclusion of this variable was warranted. For all sites, the developed models with all explanatory variables included had the lowest Press statistic. The Press statistic for Site 2 multiple linear regression model was 54.52, 58.83 for Site 3, and 68.76 for Site 1.

No multi-collinearity problems were indicated by VIF values.

Non-normality of residuals and serial correlation reduces the ability to validate the developed models but the models still have strong predictive power. The models developed for Sites 1 – 3 were applied to two storm events to further assess their predictive ability. Figure 6-4 shows that the developed multiple linear regression model for Site 2 follows closely the actual pH for validation storm event 1. The model exhibits a very similar pH dip and follows the initial phase of an antecedent period diel cycle. However the model predicts pH recovery to be much faster than actually occurs. Overall, the developed models seem to be a very good predictor of episodic acidification. Storm event 2 proves that a watershed this dynamic cannot always be predicted through statistical methods. This storm (Figure 6-5) exhibited an uncharacteristic increase in pH rather than a decrease. Figure 6-5 shows that when the minimum stream pH was supposed to be reached, pH was actually at the average base line pH. The remaining models were also applied to storm event 1 and 2 with similar results (See Table 6-4).

4.2 Discussion

The primary cause for depressed stream pH inferred from the developed models is precipitation input. The developed models were sufficient in proving that an association between precipitation input and decrease in pH exists. From this association it can be inferred that the acid input brought into the system through precipitation is a cause of

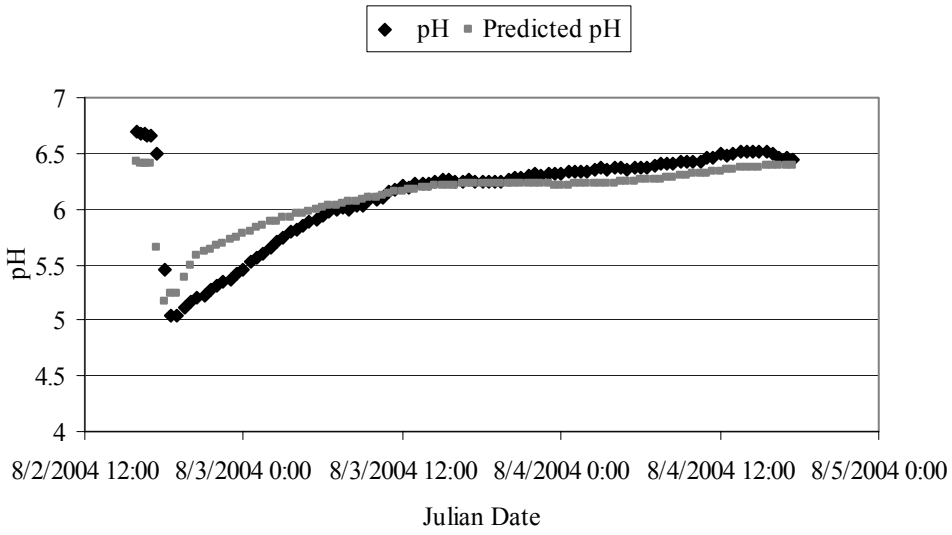

Figure 6-4. Predicted and actual pH for storm event 1 at Site 2. ($r^2 = 0.873$).

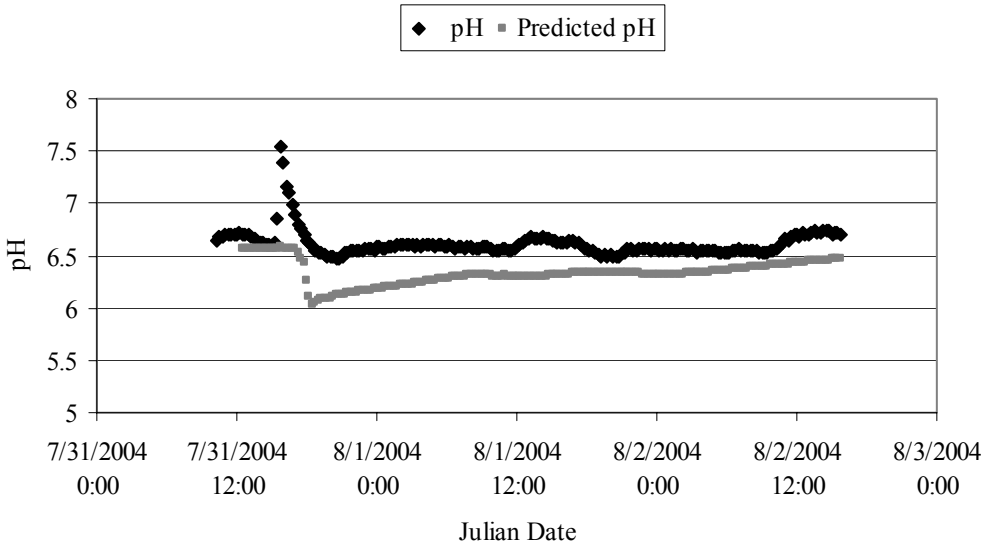

Figure 6-5. Predicted and actual pH for storm event 2 at Site 2. ($r^2 = 0.294$).

Table 6-4. Developed pH storm models applied to two validation data sets with r^2 values.

Storm Event	r^2 values		
	Site 1	Site 2	Site 3
Storm Event 1 (8-2-04)	0.78	0.87	0.85
Storm Event 2 (7-31-04)	0.43	0.29	0.20

episodic acidification. Barnett found stage, flow, and precipitation to be a significant predictor of pH (2003). However, the data used in the study was biased toward baseline stream flow. Based on the predictive ability of the constructed models and past work in the GRSM, it can be stated with confidence that precipitation input plays a major role in episodic acidification.

5. Multiple Linear Regressions for Storm Event Turbidity Prediction

Turbidity in the Little Pigeon River can be highly variable. Leaf litter and other materials can affect turbidity readings. For Site 2 the inter-quartile range (IQR) was 3.30 (NTU) and the range was 1286.60 (NTU). This implies that most of the data is well below the maximum value of 1286.90 (NTU). For the model building set over 99.5% of the turbidity data was below 100 (NTU). A plot of turbidity versus stage does not indicate a linear relationship (Figure 6-6). The extreme outlying turbidity points around 1000 NTU and elevated turbidity in the mid range of stage make it unlikely that turbidity would be able to be predicted with the available variables. To help correct for high variance two methods were explored: data smoothing and outlier exclusion.

Moving averages with various window sizes were used to help reduce the variance seen in the turbidity data. Data smoothing eliminated local trends (e.g. local maximums and minimums). The original intent was to reduce variability. This goal was achieved but at the expense of skewing baseline data higher than normal. Data

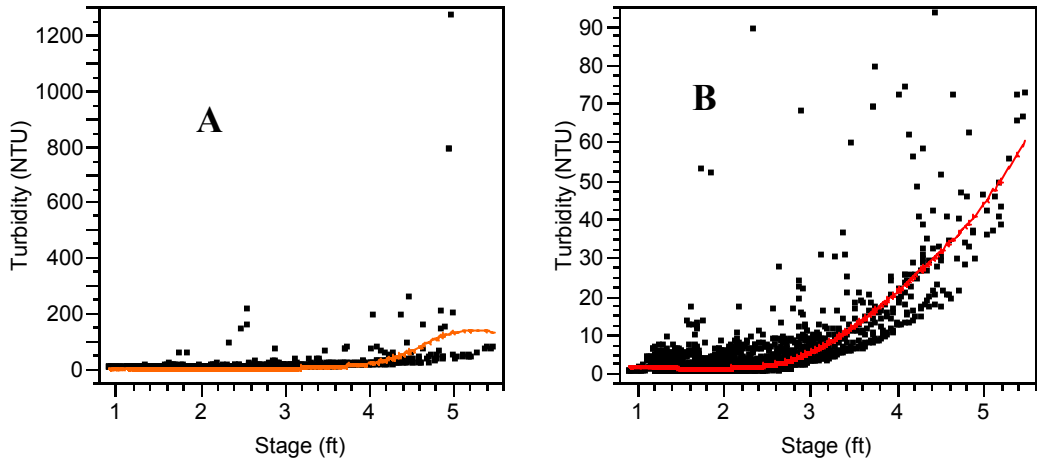

Figure 6-6. Plot of turbidity (NTU) versus stage at Site 2 with fitted spline curves (lambda equal to one). "A" has included all storm data with r^2 equal to 0.22. "B" has 14 data points above 100 (NTU) excluded with r^2 equal to 0.63.

smoothing resulted in the data being transformed so that it no longer presents an accurate picture of actual water quality.

In lieu of data smoothing, outlier exclusion was investigated. Excluding points was used with caution since no concrete physical reason exists to justify such exclusions. It was suspected that anomalously high one-time readings were due to large debris such as leaf litter. Since 99.5% of the data was under 100 (NTU) for all three sites observations higher than 100 (NTU) were excluded from the data set. For all model building data sets, fifteen or less points were excluded.

Both data smoothing and outlier exclusion were used to build storm turbidity models with similar degrees of success depending on which site was being examined. Both methods altered the data set to different extents but outlier exclusion resulted in a model that was perhaps more realistic of the water quality observed. Data smoothing skewed the data making it unrepresentative of the turbidity data set. Outlier exclusion

omitted high readings that may actually represent stream conditions. However, outlier exclusion was employed for model building.

Turbidity had a low correlation with stage but a plot of turbidity versus stage (Figure 6-6) indicated that a transformation was necessary. A spline curve was fitted to assess the general relationship and indicated that a power transformation of stage such as stage squared would improve fit. For Site 2 the r^2 was raised from 0.37 to 0.62 after adding stage squared. Sites 1 and 3 had comparable results. Higher degree polynomials did produce slightly higher r^2 values at Sites 1 and 3 but their slopes were not significant at a 95% confidence level. However, for Site 2 higher degree polynomials were significant but only slightly improved the r^2 value. In general the least complicated model that explains a satisfactory amount of variance should be chosen and a second-degree polynomial was deemed sufficient.

Stage transformed into a quadratic explains a significant amount of variance but there are several other driving forces. Rainfall intensity logically has to effect how much debris is washed into the stream. Also, rainfall intensity affects how fast the stage rises. Turbidity should be higher if a stream rises rapidly versus rising slowly. Two explanatory variables were explored to represent varying increases in stage: rainfall intensity (inches/minute) and stage intensity (ft/day). The rainfall intensity was entered into the data set by summing the amount of rainfall that fell over the fifteen minutes prior to a particular sonde reading then divided by fifteen minutes. Stage intensity is represented by the change in stage divided by the elapsed time, generally fifteen minutes. Rainfall intensity was not a significant variable when added in conjunction with stage. However, time of concentration was not taken into consideration. Stage intensity was

significant and easier to compute then time of concentration for rainfall. Site 2 r^2 value increased from 0.62 to 0.68. Sites 1 and 3 had similar results.

Intuitively the time of year should affect turbidity readings. During winter months the ground is frozen resulting in less debris being captured by storm run-off. Also, during the fall there is a significant increase in leaf litter and other organic matter that would be washed into the stream. Both occurrences occur at different times of the year thus a way to introduce this seasonal effect into the model was investigated. Sin (δ) and cos (δ) were used where δ is equal to the year fraction multiplied by 2π. For Site 2 the r^2 value was increased from 0.68 to 0.74 and Site 3 from 0.42 to 0.53. Sin and cos were not significant for Site 1 and were not used.

The developed model is shown in Equation 6-3 and model parameters in Table 6-5.

$$\text{Turbidity} = b_0 - b_1*\text{Stage} + b_2*\text{Stage}^2 + b_3*\text{Stage Intensity} + b_4*\sin(\delta) + b_5*\cos(\delta)$$

Equation 6-3

Where:

Turbidity = stream turbidity recorded by sonde, NTU
b_i = regression coefficient
Stage = stream stage recorded by sonde, ft
Stage Intensity (ft/day) = abs Δ Stage divided by Δ in time, ft/day
δ = year fraction multiplied by 2π

Table 6-5. Models parameters for storm event turbidity model.

Site Name	Regression Coefficient						Model p	r^2	N
	b_o	b_1	b_2	b_3	b_4	b_5			
Site 1	-2.25	2.98	6.51	0.21	--	--	0.0000	0.70	3099
Site 2	-2.04	2.14	4.04	0.34	-2.29	-1.10	0.0000	0.74	4144
Site 3	2.03	1.06	4.76	0.39	5.15	1.33	0.0000	0.53	2845

5.1 Multiple Linear Regression Diagnostics Results

There is no set standard for how high the r^2 value should be since models with low r^2 can still prove a relationship exists but that more variables are needed. Sites 1 and 2 had very acceptable r^2 values since over 70% of the variance was explained. Site 3 r^2 was lower indicating significantly less variance was explained. Referring to Chapter 4, the IQR was wider for Site 3 compared to Sites 1 and 2. Also the standard deviation was much larger further indicating that Site 3 turbidity was much more variable. This reduced the models ability to accurately predict turbidity.

The residuals for Site 2 model (Figure 6-7) appear to be somewhat random although serial correlation is likely to be present. Correlation of residuals with lagged residuals confirms serial correlation is present for all models. As with the pH storm model, the residuals were not normally distributed as indicated by the normal quantile plot and goodness of fit test ($p=0.0100$). (See Figure 6-8.)

Several other diagnostic tools were used. VIF values for stage and stage^2 was over ten. This was easily corrected by centering the data. The mean of stage was subtracted from stage then the regression was rerun. VIF values were less than ten indicating no multi-collinearity problems. The tools described in section 3.7 to determine presences of outliers were employed for the turbidity models. Ultimately no points could be excluded since no error in the data could be identified.

As with the pH storm models, the turbidity storm models were applied to a validation storm event to assess their predictive power. The developed statistical model for Site 2 was applied to a storm event that began on August 2, 2004. The predicted values follow the same general direction as the actual turbidity values (Figure 6-9).

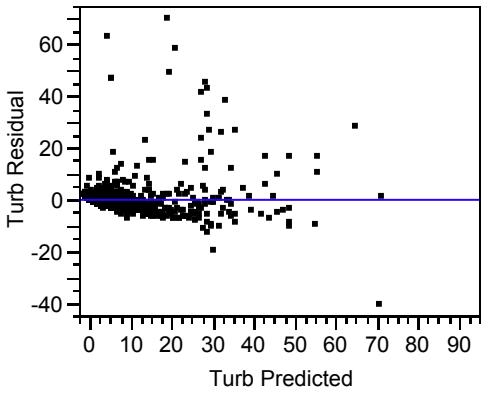

Figure 6-7. Residual plot from Site 2 turbidity storm model.

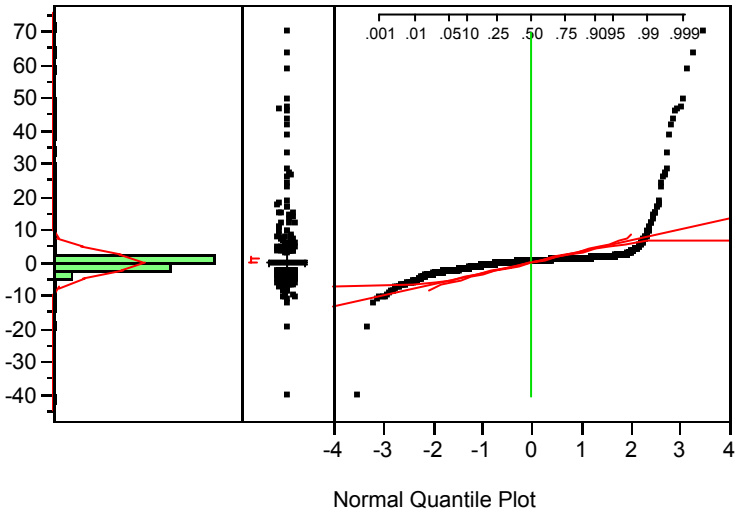

Figure 6-8. Determination of normality of residuals at Site 2 for turbidity storm model.

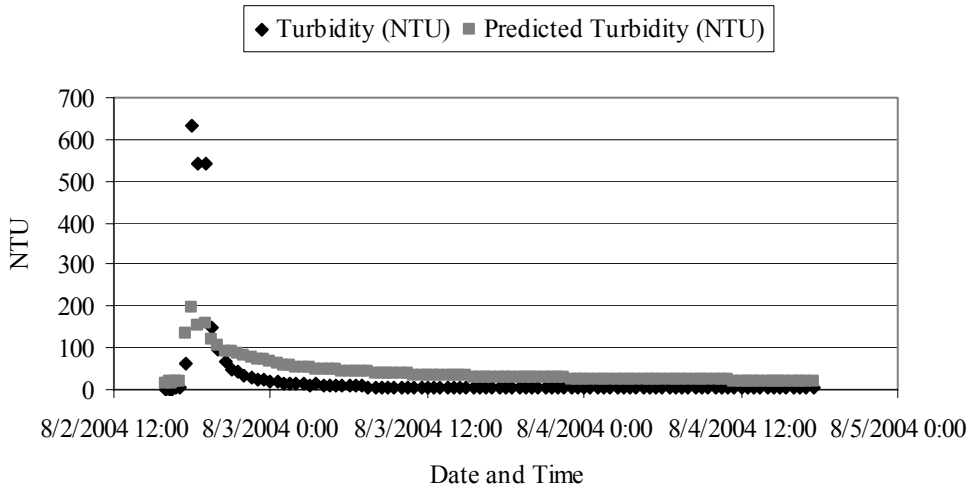

Figure 6-9. Predicted and actual turbidity for storm event 1 at Site 2. ($r^2 = 0.66$).

Likely a consequence of excluding extreme outliers, the model is unable to accurately predict the three outlying points seen in the actual turbidity. The actual turbidity also recovers faster than the model predicts. The r^2 (0.66) for this storm event is reasonable considering the outlying measurements likely have a lot of pull. The model was able to predict turbidity measurements above 100 NTU even though the model building set excluded any values above 100. The remaining statistical models were applied to the same storm event. Site 1 had a high r^2 (0.75) indicating that the model is able to predict future events. Site 3 had a significantly lower r^2 for the same storm event (0.34). Again the model is a poor fit for the highly variable data seen at Site 3.

5.2 Discussion

The model for Site 1 varied from the other two in that the time of year did not improve fit and was not a significant variable. This may represent the physical differences between the sites. The data set is only one year in length and seasonal effects may become more evident over a longer time period.

Sites 1 and 2 statistical models had satisfactorily predictive power. The r^2 values when applied to the model building and validation data set indicated a significant amount of variance had been explained. The statistical models built should provide insight to any construction period changes encountered. However, Site 3 had less variance explained warranting further investigation of the difference between the sites. This model should be applied to future data sets with caution.

6. Conclusion

Statistical models can provide valuable insight into the driving forces of many natural occurring events. The developed statistical models had a number of deficiencies including lack of normality of residuals and serial correlation. Applying the statistical models to future data sets proved that the models were able to satisfactorily predict future occurrences. On this basis data collected during construction and post-construction periods should reasonably fit the models developed for the pre-construction period. Models may also be constructed from construction and post construction for comparison to the developed models from preconstruction data. Perhaps even more important to the NPS long term is the knowledge gained into major driving forces of episodic acidification and increased turbidity. The major causes inferred from the developed models for episodic acidification were:

1. Increase in stage which is probably a surrogate for complex hydraulic phenomena occurring during a storm event
2. Total volume of precipitation

The major causes inferred for increased turbidity seen during storm events was:

1. Increase in stage with increasing effect as stage rises (represented by a quadratic polynomial)
2. Rate of stage increase
3. Time of year

Chapter VII. Other Water Quality Characteristics

1. Introduction

The watershed dynamics of the LPR watershed are complex and highly variable. There was a number of unanticipated water quality aspects noticed during the preconstruction study. This chapter will highlight three water quality aspects which illustrate the complex nature of the watershed. Diel cycles (commonly referred to as a diurnal cycle), initial upward pH spikes during precipitation events, and depressed stream pH corresponding to mean precipitation pH were observed.

2. Diel Variations

Diel variations in pH and temperature (higher values during the day and lower values at night were observed at all three sites on the Little Pigeon River (LPR) (Figure 7-1). This phenomenon was also noticed at the fourth site on Ramsey Prong but was much less distinct. Two potential causes of the diel pH variations are 1) daily temperature cycles or 2) biological activity cycles, e.g., algae photosynthesis/respiration. In order to investigate whether temperature cycles could account for the diel pH variations, geochemical equilibria modeling was performed using Visual MINTEQ Version 2.23 (Gustofsson 2004). The median base line water quality values for August 25, 2003 – May 29, 2004 for Site 1 were used as model input as shown in the table 7-1 below. Since pH can change significantly from the field to the lab, the typical base line pH of about 6.5 measured by the sonde was used rather than the median lab value of 6.22. The model was run at the median temperature of 9.8^{o}C and then ±5 ^{o}C, which was slightly greater than the maximum temperature variation seen and much more than the

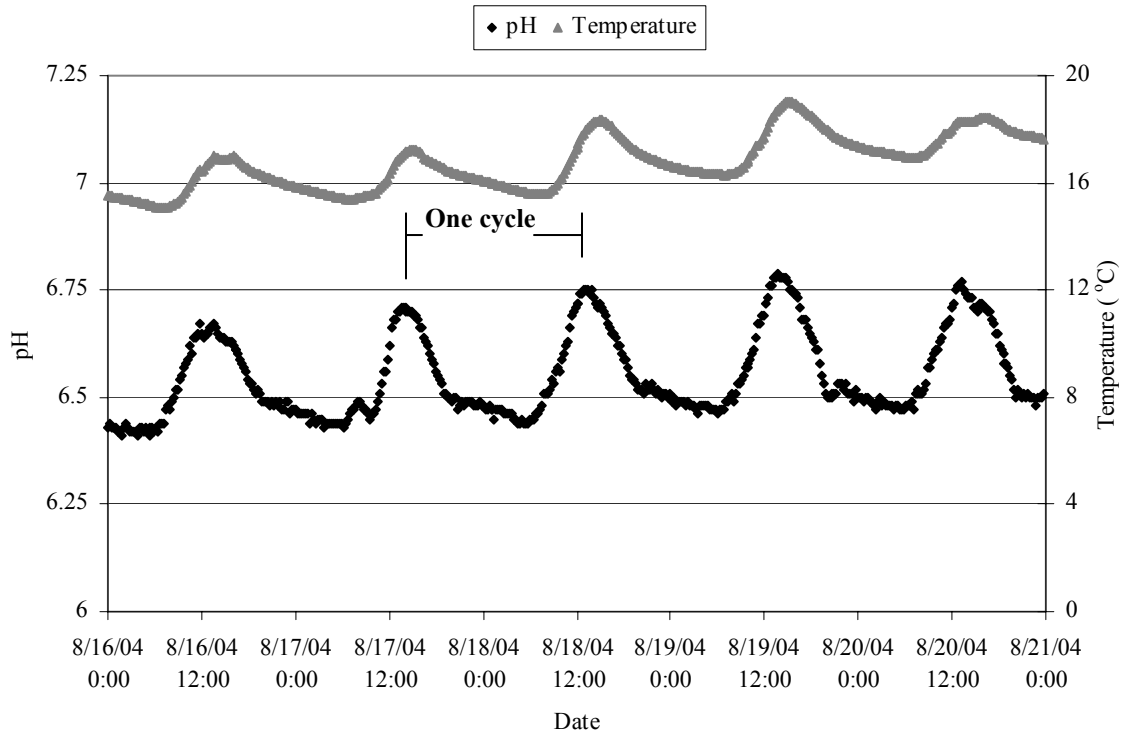

Figure 7-1. Example diel cycle observed in sonde pH and temperature at Site 1.

Table 7-1. Component concentrations for diel pH modeling.

Component	Concentration for closed CO_2 system, µmoles/L	Concentration for open CO_2 system at 9.8°C, µmoles/L
Al^{3+}	1.02	1.02
Ca^{2+}	33.9	33.9
Cl^-	13.02	13.02
CO_3^{2-}	107.55	100.39
Cu^{2+}	0.04	0.04
H^+	156.54	128.12
H_4SiO_4	89.2	89.2
K^+	11.6	11.6
Mg^{2+}	14.5	14.5
Na^+	41.1	41.1
NO_3^-	18.86	18.86
SO_4^{2-}	39.05	39.05
Zn^{2+}	0.16	0.16
Alkalinity, mg/L as $CaCO_3$	2.81	2
pH	6.22	6.808
p_{CO2}, atm	NA	0.0004
Charge difference	4.93%	9.02%

typical range of about 5 °C. The model was run for two types of systems: closed to CO_2 and open to CO_2. For the closed system, the proton and carbonate concentrations were determined by first using the median alkalinity and pH as input (along with the other component concentrations). The total proton and carbonate concentrations were then used in the subsequent modeling since they should be conserved. For the open CO_2 system, the p_{CO2} was set constant at 0.0004 atm. For the open system, it is not possible to fix pH, alkalinity, and p_{CO2} simultaneously since this over specifies the system. Rather, only two of the variables can be fixed although the measured alkalinity of 2.81 mg/L as $CaCO_3$, measured pH of 6.5, and typical atmospheric p_{CO2} of about 0.0004 atm should ideally be consistent with each other. However, this was not the case. Fixing alkalinity and p_{CO2} gave a pH of 7.00 while fixing pH and alkalinity gave a p_{CO2} of 0.001806 atm and fixing pH and p_{CO2} gave an alkalinity of 0.63 mg/L. As a compromise, a p_{CO2} of 0.004 atm, alkalinity of 2.0 mg/L and pH of 6.81 were found to be consistent and thus the alkalinity and p_{CO2} were fixed and the pH allowed to vary with temperature. Alkalinity was fixed since it should be conserved with temperature changes if there is no biological action, while the total carbonate component would not be conserved. The results are shown in Table 7-2.

As seen in Table 7-2, both the closed and open system should have the highest pH at night (lowest temperature) if temperature is the main driver of diel pH variations. This is opposite to the observed trend of higher pH during the day. Also, the maximum pH range would be about 0.11-0.18 units which is smaller than the observed pH variation of about 0.3-0.5 units seen in September and October 2003 which are typical of non-winter

Table 7-2. Results of geochemical equilibria modeling of pH vs. temperature.

Temperature, ^{o}C	Closed system pH	Open system pH
4.8	6.558	6.822
9.8	6.500	6.808
14.8	6.450	6.804

months. Therefore, temperature variation does not appear to be the main driver of diel pH variations.

Diel pH variations are commonly seen in streams including mountain streams (Nagorski et al. 2003). Such diel variations are typically attributed to biological action and are the most logical cause here as well, e.g., daytime photosynthesis could be expected to raise pH and night time respiration to lower it (Goldman and Horne 1983).

Dissolved oxygen (DO) also had a distinct diel cycle. It may be expected that DO would fluctuate due to biological activity similar to pH diel cycles discussed above. However, DO generation and consumption through algal and plant activity was most likely not the cause. Photosynthesis production of oxygen would result in peak DO being observed during the day. Peak DO was observed at night (Figure 7-2). The DO diel cycle seen is due to variation in temperature. Colder water has a higher capacity for dissolved oxygen and consequently changes in saturation vary with temperature. Equation 7-1 was used to determine the theoretical dissolved oxygen saturation at a given temperature (Chapra 1997). Graphing theoretical saturation with actual DO illustrates two things. The DO probe was not calibrated properly since actual DO is about two mg/L above theoretical dissolved oxygen saturation. It also shows that the theoretical

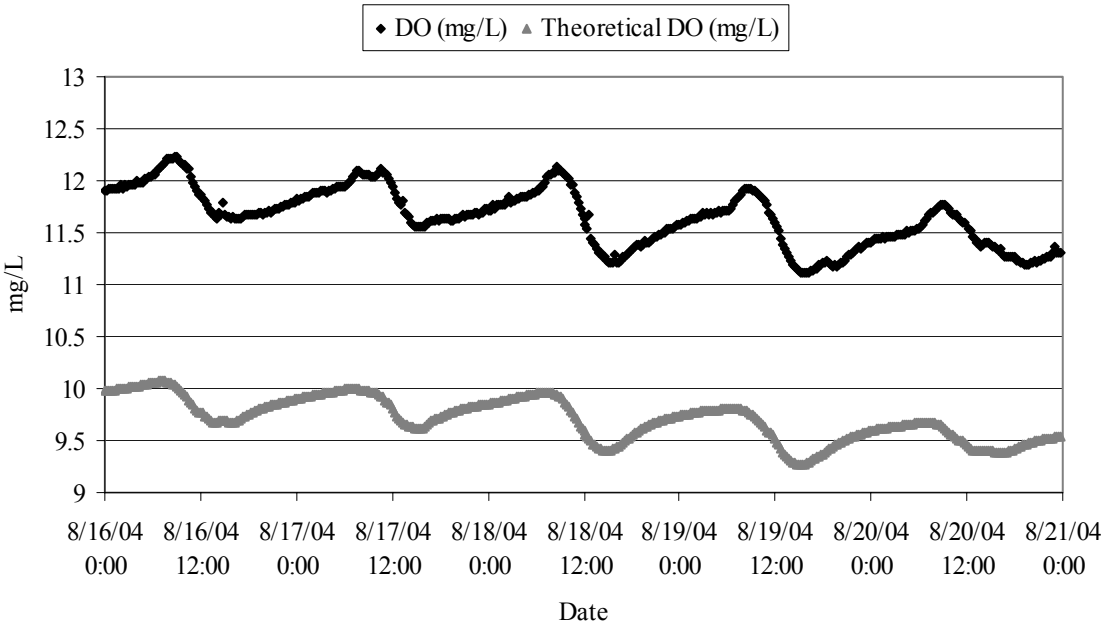

Figure 7-2. Diel cycle example for temperature and dissolved oxygen at Site 1.

and actual DO trend together very well. The Pearson r correlation coefficient for actual and theoretical DO was 0.91 indicating that the DO diel cycle was due to the temperature diel cycle.

$$\ln O_{sf} = -139.3411 + \frac{1.575701\times10^{5}}{T} - \frac{6.642308\times10^{7}}{T^{2}} + \frac{1.243800\times10^{10}}{T^{3}} - \frac{8.621949\times10^{11}}{T^{4}}$$

Equation 7-1

Where:

O_{sf} = Theoretical dissolved oxygen saturation (mg/L)
T = Temperature (K)

A slight diel variation in conductivity was also observed. The sonde has a maximum resolution of 1 μS/cm for conductivity thus minute changes were not perceptible. However when changes occurred, conductivity was lower during the day and higher at night (Figure 7-3). This supports biological activity being the driving force since increased respiration (greater effect at night) should cause an increase in conductivity (Bourg and Bertin 1996). Other sites during different time periods also exhibited this slight diel cycle in conductivity. This conflicts with a previous GRSM study that found no diel cycle in conductivity although the study did not have the benefit of 15 minute sonde readings (Silsbee and Larson 1982).

3. Initial pH Increase in Storm Events

Examination of sonde pH at all four stream sites revealed that rapid pH increase is a common occurrence at the onset of a storm event. A 2.07 increase in pH was observed at Site 1 in response to a storm event on September 3, 2003. However, increases were generally one pH unit in magnitude. (This occurred less frequently at Site 4.) This goes

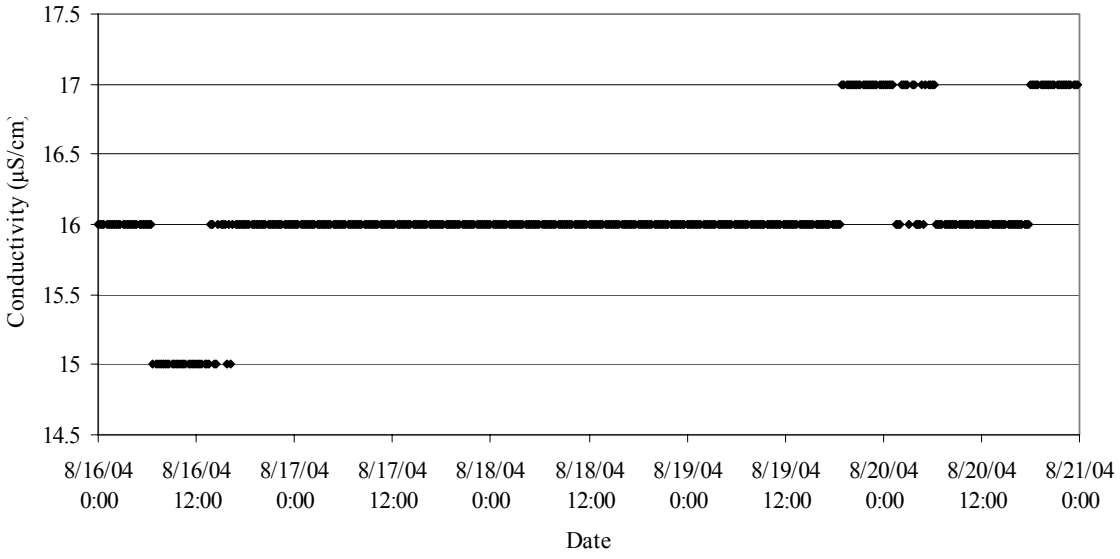

Figure 7-3. Slight diel variation in conductivity at Site 1.

against the well established trend of pH decreasing with the input of precipitation. Figure 7-4 illustrates a typical upward pH spike at Site 2 followed by an archetypical decrease in pH. The sequential precipitation collector provided some insight to this phenomenon. The sequential precipitation collector results at Site 6 during the same storm event found that precipitation pH was variable. The highest pH was at the beginning of the storm event and the lowest seen in the last sample captured (Figure 7-5). This increase in pH is undoubtedly related to the increased ANC (acid neutralizing capacity) seen during the beginning of the storm event in the precipitation samples collected. The first sample collected by the sequential precipitation collector had an ANC of 125 μeq/L which is well above the average stream baseline ANC concentration of 62 μeq/L at Site 2 (Figure 7-6). The last precipitation sample collected had zero ANC which is typical of bulk rain precipitation samples commonly collected during this study and previous GRSM studies. This supports the argument that the first flush phenomenon increases stream pH since after the first flush has occurred, ANC and pH decrease in the stream and precipitation.

Figure 7-4 illustrated a typical stream pH increase that stayed above mean pH for 1.5 hours with a stage increase of approximately 1.6 feet. The stream pH then decreased as expected. Storm stream samples were also captured by auto-samplers on July 31, 2004. This storm had a stage increase of about 1.6 feet but had an atypical 1.12 increase in stream pH that endured for three hours (Figure 7-7). The captured storm stream samples provided insight into this pH increase. An increase of pH is generally associated with an increase in ANC. A large increase in stream ANC above mean ANC was observed (Figure 7-8). As equation 7-1 shows, an increase in carbonate or bicarbonate pushes the chemical equilibrium of the carbonate system to the left. This causes

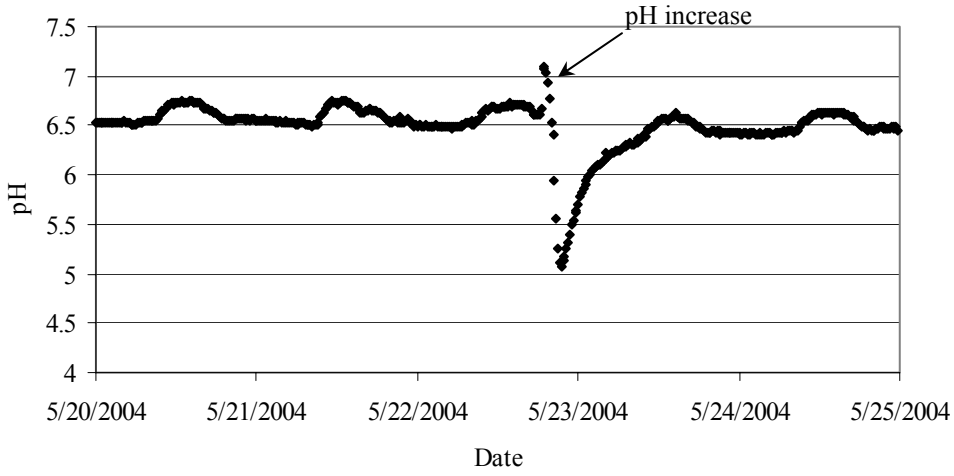

Figure 7-4. Sonde pH spike example at Site 2.

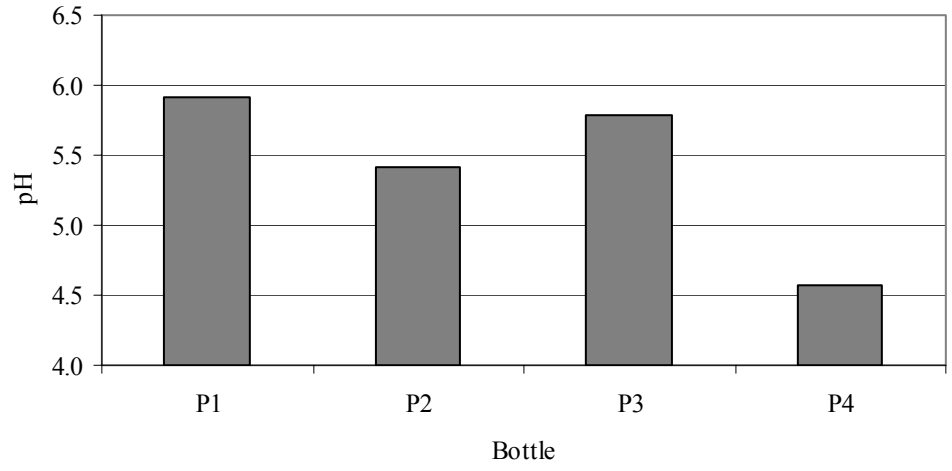

Figure 7-5. Varying pH during a storm event beginning May 22, 2004 at Site 6.

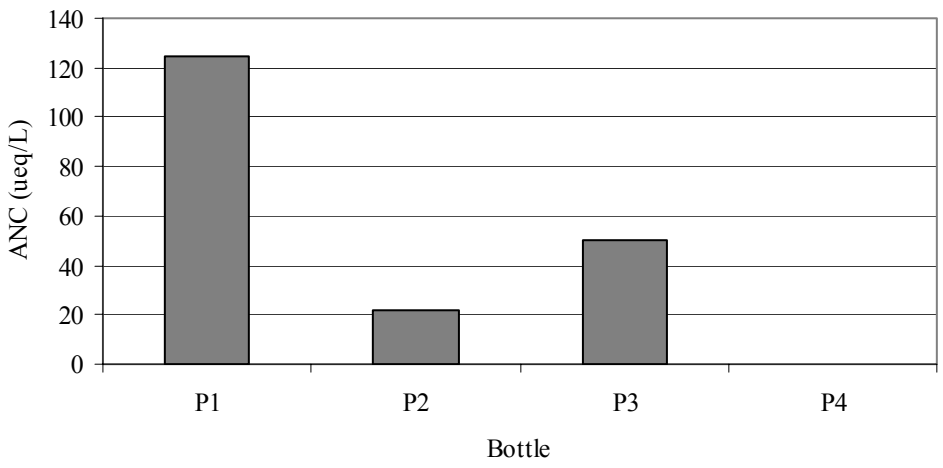

Figure 7-6. Varying ANC during a storm event beginning May 22, 2004 at Site 6.

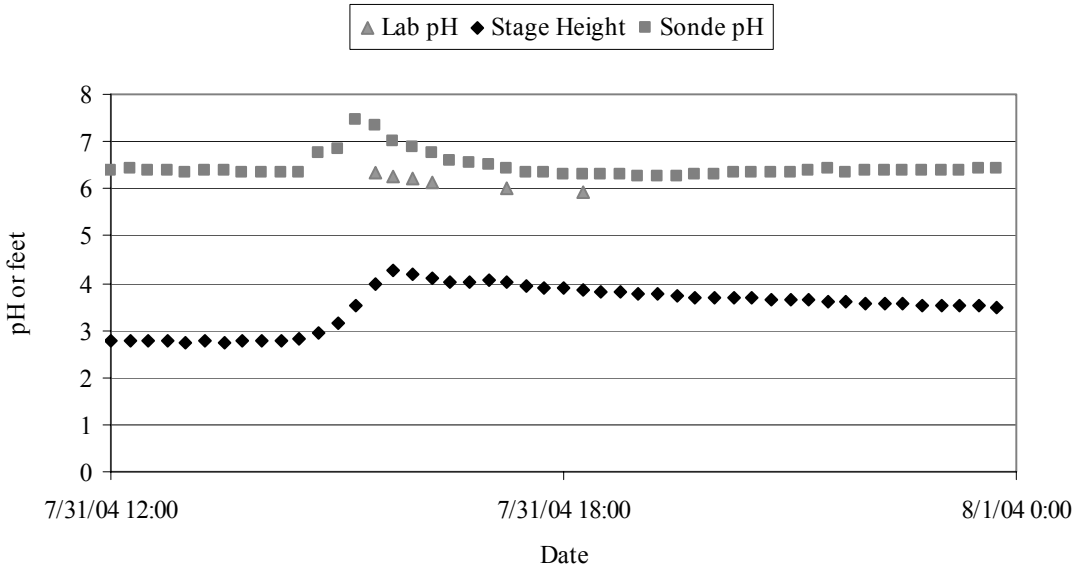

Figure 7-7. Atypical stream pH increase at onset of storm event at Site 3.

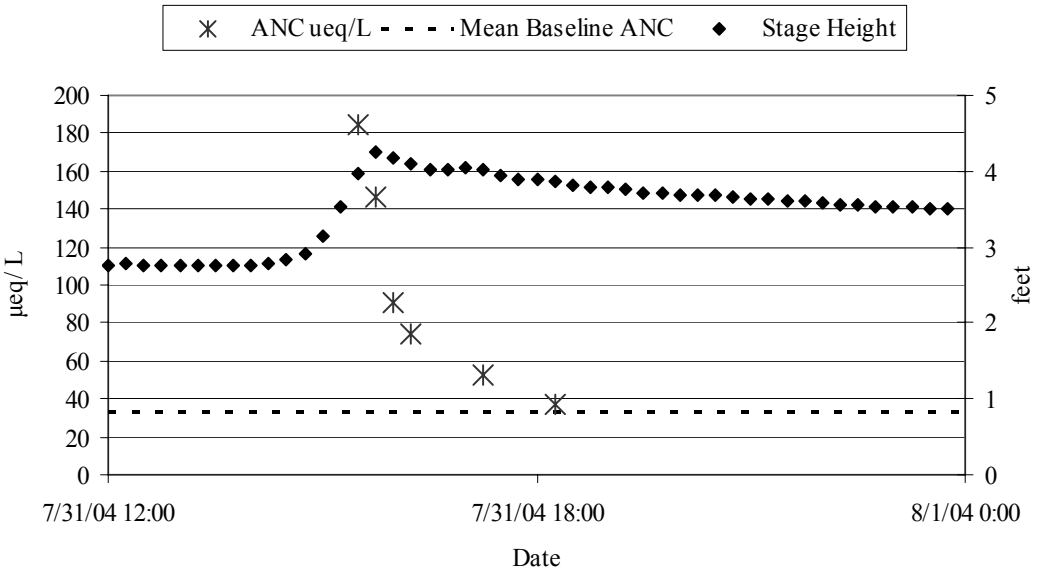

Figure 7-8. ANC increase at onset of storm event at Site 3.

hydrogen ions to be consumed thus raising the pH.

$$H_2CO_3^* \leftrightarrow HCO_3^- + H^+ \qquad \text{Equation 7-1}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

To maintain the charge balance and explain the increase in pH, a significant increase in anions must be accompanied by an increase in cations. There is a significant similar magnitude increase in stream calcium as illustrated in Figure 7-9. Rearrangement of an ion balance yields:

$$[H^+] \text{ (μeq/L)} = \sum \text{Anions (μeq/L)} - \sum \text{Cations (μeq/L)} \qquad \text{Equation 7-2}$$

Where:

$[H^+]$ (μeq/L) = stream hydrogen ion concentration
$\sum$ Anions (μeq/L) = sum of all negatively charged ions
$\sum$ Cations (μeq/L) = sum of all positively charged ions except hydrogen

Equation 7-2 shows that an equal increase in cations and anions will not produce a pH change. In order for the pH increase seen in Figure 7-7 to occur the sum of the cations must increase slightly more than sum of the anions. In general there is a greater increase in cations than anions but the slight difference in the sums in Equation 7-2 to calculate pH is not possible within the precision of instruments.

The first sample collected by the sequential precipitation collector collected on July 27, 2004 showed calcium concentration of 222 μeq/L and ANC concentration of 139.94 μeq/L. Subsequent precipitation samples decreased in calcium and ANC. This supports the first flush concept in which substances accumulate during antecedent periods and are carried into the stream through run-off. This same accumulation likely occurs on the sequential precipitation collection funnel resulting in initial increase in ions.

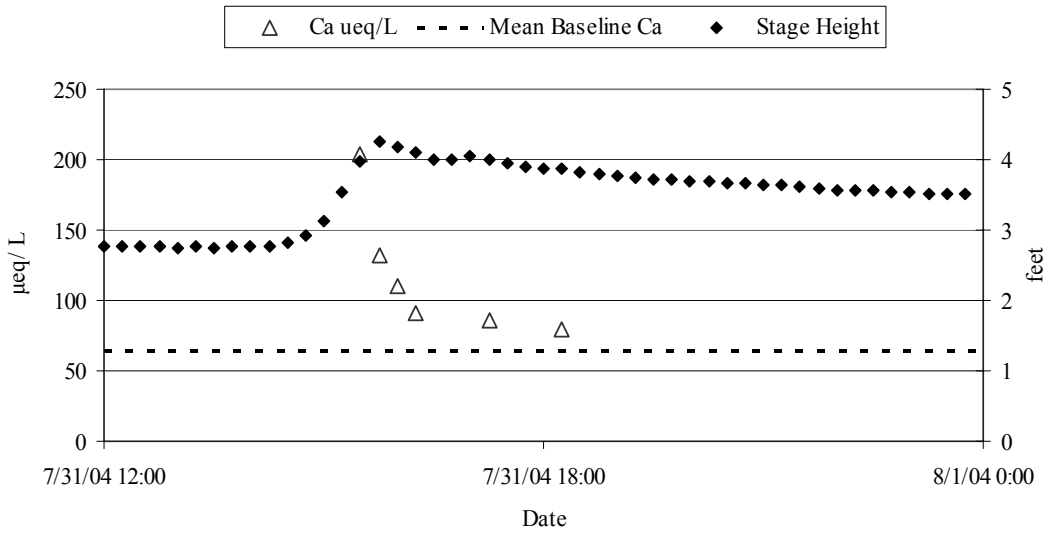

Figure 7-9. Increase in calcium at onset of storm event at Site 3.

4. Comparison of Minimum Stream pH to Precipitation pH

Episodic acidification is a well documented occurrence associated with precipitation input. Previous sections used statistical methods to explore this relationship but this section will take an intuitive look at the relationship between stream and precipitation pH. Since precipitation is believed to play a major role in depressed stream pH it is logical to expect stream pH to drop to pH commonly seen in precipitation samples if the event is large enough to overpower any attenuation capacity of the watershed. However the minimum stream pH seen at Site 2 was 5.04 which does not correspond to the bulk precipitation pH of 4.30 collected for that storm. The mean sequential precipitation pH for that storm event was 5.16. The stream pH is closer to the sequential mean pH than to the bulk precipitation pH. This seems to indicate that bulk precipitation water quality alone does not explain the minimum stream pH. A look at multiple storm events finds that the stream pH often depresses to around 5.0 (see Figure 7-10). In two of the depressed pH events, stream pH is closer to sequential pH than bulk precipitation pH. A relationship between stream pH and sequential precipitation pH seems to exist. The second episodic event in Figure 7-10 does not correspond very well to either precipitation pH. The sequential precipitation pH is lower than normal and the stage increase is not as great the other two events.

5. Conclusion

There has been several interesting water quality aspects presented in this chapter. The conclusions drawn from this chapter are:

- pH and conductivity diel cycles are most likely due to biological respiration and photosynthesis

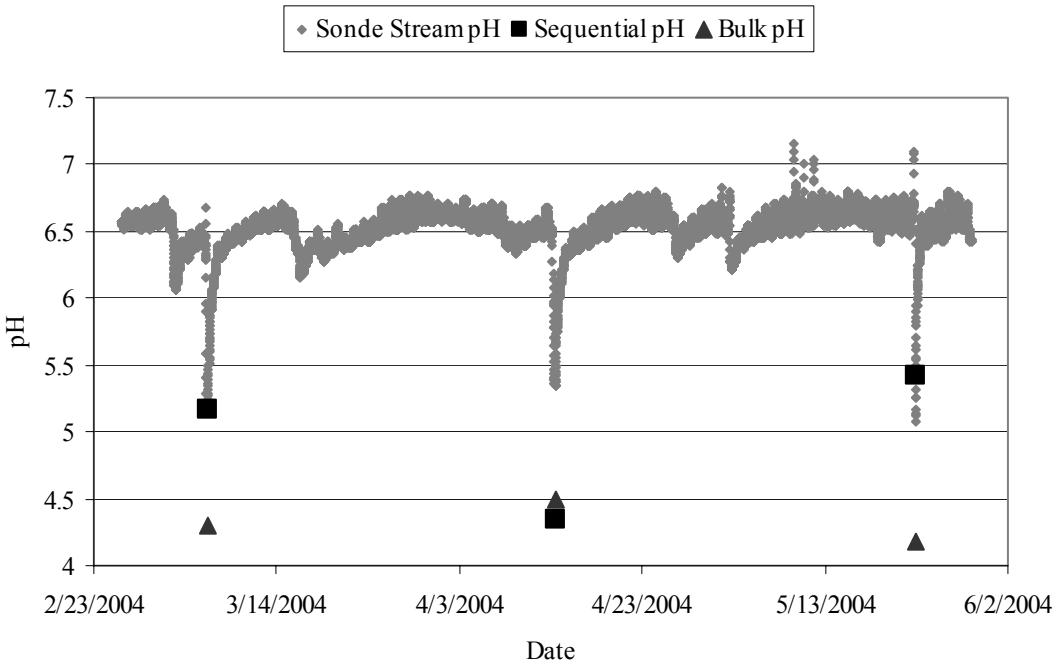

Figure 7-10. Stream pH depression associated with mean precipitation pH at Site 2.

- Stream temperature diel cycles are due to change in air temperature
- Dissolved oxygen diel cycles are due to stream temperature variation
- Accumulation of ions during antecedent periods may cause stream pH increase
- Minimum stream pH corresponds well to sequential precipitation pH

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Vitae

James Chadwick Roby was born in Owensboro, KY on December 29, 1978. Chad was fortunate enough to be raised by his grandparents, Jim and Sarah Trogden, in Yelvington, KY. Chad also has a very loving mother, Sandra Gayle Trogden and four wonderful sisters: Nicole, Amanda, Kim, and Sarah. In latter years, he developed good relationships with his two older brothers Chris and Andy.

Chad graduated high school from Daviess County High School in Owensboro, KY. With motivation and dedication he graduated from Murray State University with a Bachelor of Science in Environmental Engineering Technology "Magna Cum Laude." In Chad's junior year he took a break from school to join the United States Army Reserve. He graduated from Advanced Individual Training first in his class. Being in the army and going through "boot camp" were valuable experiences and undoubtedly shaped his life for the better. His favorite motto comes from the Army, "Adapt and Overcome." With continued drive and determination this vitae lies within the final step towards completing his Master of Science degree in Environmental Engineering from the University of Tennessee.

Chad played the trumpet in concert and marching bands from elementary school through college. He enjoys outdoor activities such as hiking, biking, running, spelunking, and rafting. Working on a Great Smoky Mountain National Park project provided him the opportunity to spend a great deal of time in the Smokies and many fond memories were gained from working in the park Chad also enjoyed hiking to all the waterfalls in the park with friends and family.

Chad plans on next pursuing of Doctor of Philosophy degree and registration as a professional engineer. After a few years of working, Chad plans to pursue a career in academia.