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I am submitting herewith a thesis written by Thomas Wayne Barnett entitled “Stream Water Quality Modeling in 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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Stream Water Quality Modeling in the Great Smoky Mountains National Park

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Abstract

The purpose of this study was to examine water quality in the acid-impacted Great Smoky Mountains National Park (GRSM). Water samples have been collected roughly quarterly at ninety sampling sites throughout the Park. These samples were analyzed for pH, acid neutralizing capacity (ANC), conductivity, major cations, and major anions. This thesis utilizes data from samples collected from October, 1993 to November, 2002.

The trout fisheries of the GRSM are considered some of the best in the eastern United States. However, fisheries biologists at the GRSM believe that some of the streams that once supported trout populations twenty or thirty years ago, no longer do. This thesis outlines and quantifies surface water quality conditions that might be harmful to trout populations through a literature review. This thesis identifies 71 sites (79% of total sampling sites) that currently have a median pH of greater than 6.0, above which, is unlikely to be harmful to trout species unless a high runoff of acid, Al-rich water creates a mixing zone where $\text{Al}(\text{OH})_3$ precipitates. The precipitate can accumulate on the gills and impede normal diffusion of O_2 , CO_2 , and nutrients. There are 17 sites (18%) that have median pH values in the 5.0 to 6.0 range. This range of pH values is likely to be harmful to trout species when aluminum concentrations exceed about 0.2 mg/l. The lower end of this range is probably harmful to the eggs and fry of trout and also to non-acclimated trout especially when calcium, sodium, and chloride concentrations are low. The mechanisms adversely affecting trout in this range are ionoregulatory dysfunction and respiratory stress. Only two sampling sites have median pH values in the 4.5 to 5.0

range. This pH range is likely harmful to eggs, fry and adult trout, particularly in the soft water conditions prevalent in the GRSM. Ionoregulatory dysfunction, respiratory stress, and circulatory stress are the mechanisms that affect trout in this pH range. Currently, there are no sampling sites with median pH values less than 4.5, although pH values could be lowered by more than one pH unit during high-flow episodic events depending on the ANC in the stream. About 38% of the sampling sites have median ANC values in the 50 to 200 microequivalents per liter which the EPA classifies as sensitive. About 54 % of the sites have ANC in the 0 to 50 microequivalents per liter range which the EPA classifies as extremely sensitive. Four percent of the sites are classified as acidic (ANC < 0). Only three percent of the sites have ANC above 200 microequivalents. These low ANC conditions raise concerns that GRSM waters are susceptible to very low pH in storm events and continued acid deposition.

This thesis uses water quality data to investigate elevational trends. Significant ($p < 0.05$) decreasing elevational trends, i.e., decreasing values with increasing elevation, were found for pH, ANC, sodium and potassium. Significant ($p < 0.05$) increasing elevational trends were found for nitrate and sulfate. These trends proved to be quite stable with time when compared to earlier results, which used 1993 to 1998 data. No elevational trends were found for chloride, calcium, and magnesium.

Stepwise multiple linear regression was used to model pH, ANC, nitrate and sulfate. This thesis incorporates basin characteristics, time, acid deposition data, USGS stream flow data as surrogate hydrologic data, and precipitation data, e.g., inches of rain on preceding days, to determine whether these variables are associated with water

quality. Each of these variables were found to be statistically significant ($p < 0.05$) influencing factors to water quality, particularly pH. Water quality conditions were adversely affected by increased stream flows, acid deposition and precipitation. Models for pH and ANC produced R-square values around 0.71 and 0.86, respectively. Nitrate and sulfate modeling produced R-square values around 0.30.

This thesis also analyzes temporal trends in pH. Modeling reveals statistically significant decreasing trends in pH with time. If conditions remain the same and past trends continue, models suggest that 30.0 % of the sampling sites will reach pH values less than 6.0 in less than 10 years, 63.3 % of the sites will reach pH values less than 6.0 in less than 25 years, and 96.7 % of the sites will reach pH values less than 6.0 in less than 50 years. The models used to predict future pH values explain around 70 % of the variability in the data.

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Chapter I. Introduction

Description of Study Area

The Great Smoky Mountains National Park (GRSM) was officially dedicated in 1940. The GRSM is located on the border of Tennessee and North Carolina. The GRSM is the second largest National Park in the Eastern United States, comprising about 220,000 hectares (850 square miles). The park receives approximately 10 million visitors per year, making it the most visited National Park. The GRSM also receives some of the highest acid depositional rates of any park in North America raising serious concerns for stream impairment. There are more than 3000 kilometers (1860 miles) of streams in the GRSM, which support a great number of fish species, amphibians, and benthic invertibrae.

Description of Parkwide Water Quality Monitoring

Parkwide water quality monitoring began in 1993 and continues to the present. From 1993-1995, samples were collected at 367 sites semi-annually. In 1995, the number of sites was reduced to 160 and collected on a monthly basis. In 1997, the number of sites was again reduced to 90 and collected quarterly, and has continued to the present. Figure 1-1 is a map showing the locations of the ninety sampling sites. Analyses conducted for this thesis will utilize data from these ninety sites collected from October, 1993 to November, 2002 (Robinson et al., 2002).

Objectives

The trout fisheries of the GRSM are considered some of the best in the eastern United States. However, some of the streams that once supported trout populations

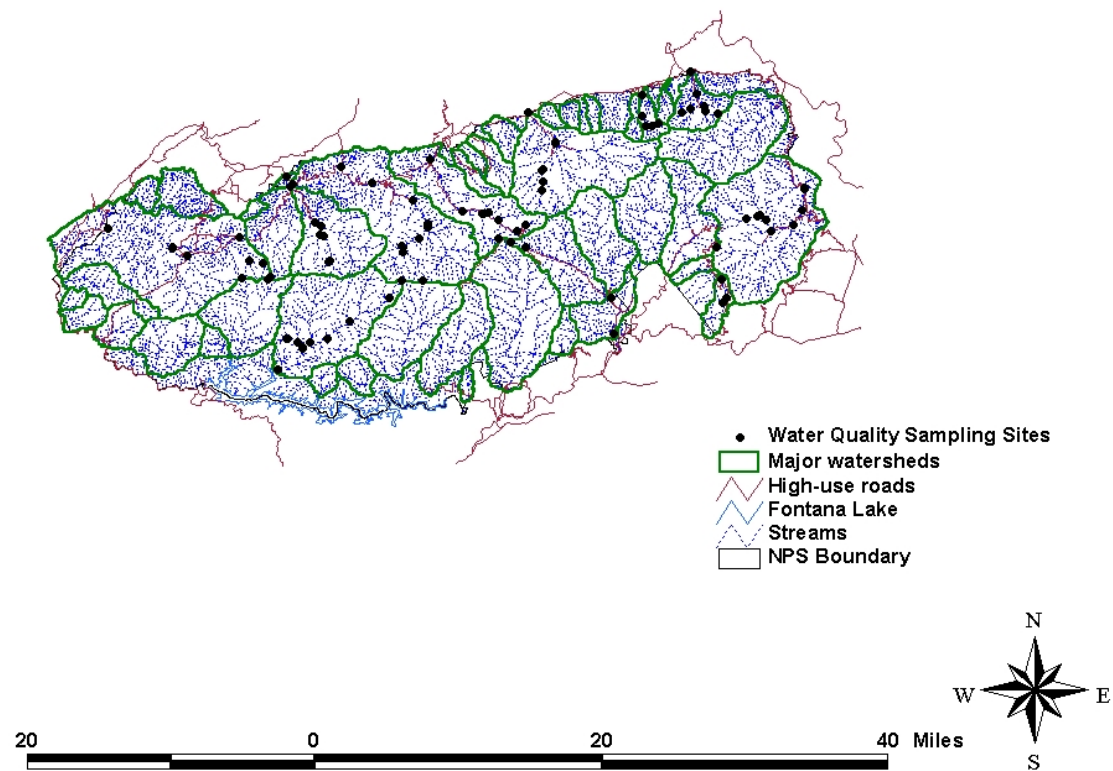


Figure 1-1. Map of water quality monitoring sites

twenty or thirty years ago no longer do. This thesis will outline and quantify surface water quality conditions that might be harmful to trout populations through a literature review. This thesis will determine the number of sites that could be of concern based on median water quality and criteria found in the literature review and also compare to Glenn Harwell's results, which used 1993-1998 data. This thesis will use an additional four years of water quality data not available to Harwell to update elevational trends and compare to Harwell's earlier results to determine how stable the trends are with time. Also, recently acquired calcium and magnesium data will be used to determine elevational trends. Stepwise multiple linear regression will be used to model water quality constituents. This thesis will incorporate USGS stream flow data as surrogate hydrologic data and incorporate precipitation data, e.g., inches of rain on preceding days, to determine whether hydrologic conditions are associated with water quality and can improve regressions. This thesis will determine whether more of the variability in time trends can be explained by incorporating stream flow and precipitation data and to use more advanced time series analyses in analyzing. The results of this thesis will hopefully be a valuable tool for the National Park Service in identifying areas of concern to trout populations based on water quality.

Chapter II. Literature Review

Pollution Effects and Criteria for the Family Salmonidae

The streams within the boundaries of the Great Smoky Mountains National Park (GRSM) are home to a wide variety of aquatic organisms that are affected by a number of natural and anthropogenic sources of pollutants. However, to limit the scope of this literature review, three species of trout, specifically the brook (*Salvelinus fontinalis*), the brown (*Salmo trutta*), and the rainbow (*Oncorhynchus mykiss*), have been selected to discuss in detail because of their sensitivity to pollution and their significance to the fisheries of the GRSM. The following review will examine several forms of pollution affecting these species with an emphasis on acidity.

Acid Pollution

Acid deposition has become a common problem in industrialized countries around the world. It may fall as rain or snow, be swept by vegetation from clouds and fog, or deposited by dry gases and particulates. Sulfuric and nitric acids formed in the atmosphere from emissions of coal-fired power plants, automobiles, etc. are of major concern. The deposition of these acids, in conjunction with other mechanisms, lowers the pH of many natural surface waters that have low buffering capacities. This reduced pH has varying physiological effects at different life stages of salmonids, and therefore, a life-cycle approach beginning with spawning will be used to consider the effects of acid pollution.

Spawning

The inability to lay eggs by mature adults subjected to chronic low pH has been noted in many studies involving both salmonid and non-salmonid species, and some reduction in numbers of eggs laid has been seen at nearly any pH below control levels of pH 7 (Heath, 1995). However, reduced egg production due to lowered pH is also highly dependent on environmental calcium levels; the lower the calcium, the fewer eggs produced (Parker and McKeown, 1987). Low environmental calcium concentrations at low pH values correlates to lower plasma calcium levels in many fish species. The effect of reduced plasma calcium at low pH values is thought to inhibit the formation of vitellogenin, which is a phosphoprotein synthesized in the liver that is transported to the ovaries as a calcium-vitellogenin complex for use in yolk synthesis (Heath, 1995). A recent study measuring vitellogenin in rainbow trout exposed to three pH levels (7.6, 5.6, and 4.5) during spawning has shown a surge in vitellogenin during a 20-day exposure period for the pH 7.6 and 5.6 groups, but no surge for the pH 4.5 fish (Roy et al., 1990). Limited data suggests that a reduction in plasma calcium of fish subjected to low pH is not due to reduced calcium uptake from the environment because low pH alone does not affect the activity of Ca^{2+} ATPase, which is responsible for calcium transport in the gills, rather it appears that increased calcium loss from the body may be more important (Parker and McKeown, 1987). Therefore, higher environmental calcium levels may compensate for an increased calcium efflux from the body.

Another hypothesis attributes reduced body size of fish due to the stress of exposure to low pH as the cause of reduced egg production. The stress (to be discussed

in a latter section) is reflected as a net loss of plasma sodium and chloride and decreased feeding, which can precipitate a severe reduction in body size (Harvey and Jackson, 1995). A study with brook and rainbow trout in soft acid water observed that egg production per unit body weight was in fact normal but that egg production was less fruitful due to decreased growth in the female (Mount, 1988). And to compound the problem, another study has found that exposure of rainbow trout females or males to acid waters (pH 4.5-5.5) during reproductive maturation causes the subsequent eggs and larvae to be more sensitive to low pH (Weiner et al., 1986).

Another effect of low pH has to do with the selection of spawning or redd sites. It has been documented that fish, in particular, and possibly other species, can sense the pH of their environment in so far as they can avoid areas of low pH (Havas and Rosseland, 1995; Alabaster and Lloyd, 1980). Significant downstream movements of brook and brown trout to avoid low pH conditions brought on by acid episodes have been documented in Linn Run in southwestern Pennsylvania (Gagen and Sharpe, 1987; Sharpe and Gagen, 1992). Studies have shown that brook trout avoid waters of pH 4.5 when selecting spawning sites and that streams with adequate spawning gravels are unable to support trout populations at pH 4.8 (Perry, 1983). Also, brook trout have been shown to select areas of alkaline upwellings from groundwater in which to build their redds (Heath, 1995; Curry and Noakes, 1995). Therefore, trout species may have to settle for less than ideal redd sites in order to avoid low pH, which can lead to reduced egg production and survival.

Egg Through Hatching

The sensitivity to acid changes as embryonic development of the egg proceeds, with the most sensitive stage being early cleavage before organ development occurs (Peterson et al., 1982). During this period the embryo's outer membrane or chorion acts as reservoir to hydrogen ions rather than a barrier, which allows diffusion of H^+ into perivitelline fluid which surrounds the embryo. As the embryo continues to develop, the chorion becomes less permeable to hydrogen ions, which increases the egg's resistance to acid waters by about 0.5 pH units (Heath, 1995). The effects of low pH at this stage can include abnormal development of various organs such as gills, brain, and heart (Peterson et al., 1982). Also, upon hatching the protective nature of the chorion is lost making the hatchlings more susceptible to the effects of acidic waters.

Another possible effect of low pH upon the hatching process is the inhibition of the chorionase enzyme, which acts as a catalyst to soften the egg capsule to allow hatching of the larvae. However, it is not known whether low pH directly affects the inhibition of the enzyme or if it is due to reduced embryo activity because of the effects on development mentioned above (Heath, 1995).

Several studies have documented survival statistics on trout eggs exposed to low pH waters. Kwain (1975) found that no rainbow trout eggs survived at pH values less than 4.5, but that there was a reasonable survival above pH 5.0. Menendez (1976) found reduced viability of brook trout eggs at pH values below 5.1 (Alabaster and Lloyd, 1980). Laboratory experiments measuring brook trout response to pH showed that egg-to-larva survival at pH 5.2 was sixty-nine percent of the survival at pH 6.5 (Marschall and

Crowder, 1996).

After Hatching Through Swim-up

Newly hatched trout are referred to as alevin. They somewhat resemble tadpoles because of the pendulous yolk sacs protruding from their undersides. Alevin remain in the protective gravel of the redd as they use up the stored nutrients in the yolk sac. Upon depletion of the yolk sac, they emerge or “swim-up” from the gravel and are then referred to as fry (Carlander, 1969).

During this period, the physiological process most affected by low pH is probably ionoregulation. A marked uptake of sodium, potassium, and calcium normally occurs during the larval development of a wide variety of species. This uptake is apparently facilitated by mitochondria-rich cells, often called chloride cells, in the yolk-sac epithelium, gills, and skin. Studies have demonstrated that brook trout fry exposed continuously to acid water (pH 4-5.2) from fertilization to swim-up failed to take up ions at the normal rate (Heath, 1995). This ionoregulatory failure is probably due to the stress presented by a low pH environment, but it's influence is highly dependent upon the environmental calcium concentration. At a pH of 4.8, a calcium level of 8 mg/L provides almost complete protection from the acid in regards to electrolyte uptake (Heath, 1995).

A possible explanation of ionoregulation problems has to do with cellular osmotic disruptions of the chloride cells due to stress. This disruption can lead to cellular swelling or shrinkage, thus affecting membrane permeability. For fish to maintain their vital physiological functions, these cells must regulate their volume after any cellular volume disruption. Most swelling cells regulate their volume by activating K^+ , Cl^- , and

organic osmolyte efflux with an accompanying loss of cellular water. This mechanism is called regulatory volume decrease (RVD). Ca^{2+} is suspected to affect this RVD response to swelling, but its exact role is still a matter of debate. In several tissues, cell swelling induces an increase in intercellular calcium which is obtained from internal stores and/or from uptake from the environment. Recent experiments on cultured trout gill cells suggest that intercellular calcium appears to be involved in volume regulation after cell swelling. The RVD response to swelling was found to be inhibited in low Ca^{2+} or Ca^{2+} free bathing solutions (Leguen et al., 2001). And since calcium is usually low in waters that are impacted by acid, alevins will exhibit a status most dependent upon the pH of the challenge (Heath, 1995). However, other studies on strains of brown trout having different sensitivity to acidic waters seem to indicate differences in calcification rate at the alevin stage. In spite of a comparable total body Ca, the strains most resistant to low pH had the lowest calcification rate of finrays and skeleton (Havas and Rosseland, 1995). This indicates that more acid resistant strains have a greater ability to draw calcium from internal stores instead of relying on outside calcium sources.

Also, ambient concentrations of the ions being absorbed seems to be important in this stage of development. Higher environmental concentrations of sodium, chloride, etc. serve to compensate somewhat for their loss. Addition of sodium chloride to raise the sodium content of a soft water from 1.65 mg/l to 14.4 mg/l increased the survival of brown trout alevins from 30 percent to 83 percent at a pH of 4.9 (Alabaster and Lloyd, 1980).

Juvenile and Adult

The effects of acid on juvenile and adult salmonid species are numerous and are dependent upon many environmental factors. Low pH affects changes in the blood of fish species and can be categorized into those occurring from acute exposure to low pH and those from chronic exposure.

Acute exposures to low pH principally occur during the early stages of snowmelt and after rainstorms following prolonged dry periods and it is estimated that these short-term events affect a greater number of fish than chronic exposures (Allin and Wilson, 2000). In areas of high acid deposition, the melt water and rain water themselves are quite acidic, but they also serve to mobilize other acid species that had been deposited by clouds, fog, dry gases and particulates. The runoff from these events can greatly depress the pH of the receiving streams and significantly affect the aquatic organisms therein, albeit for short periods of time.

There are numerous studies that show considerable drops in blood and/or whole body electrolytes of fish acutely exposed to low pH. The ionoregulation of sodium and chloride ions by the gills seems to be most affected by the stress. As the pH of the environment drops, the influx of sodium and chloride ions across the gills decreases and the efflux is greatly increased so that there is significant net loss from the fish (Gagen and Sharpe, 1987). Studies have shown that the influx of ions progressively decreases with pH, while the efflux progressively increases so that the influx is near zero at a pH of approximately 4 and the efflux is increased almost threefold over that of controls at pH 7 (Heath, 1995; Packer and Dunson, 1970). The decrease in sodium influx is thought to be

due to competition of hydrogen ions with sodium ions for the transporter at the gill.

While the decrease in chloride influx might be due to the depletion of bicarbonate and hydroxyl ions, which chloride is normally exchanged for, in the gill cells of fish in low pH waters (Heath, 1995). The increased efflux of these ions is thought to be caused by the loss of calcium from important binding sites in the gill epithelium, which affects the membrane permeability causing ionoregulatory disturbance and loss of ions (Havas and Rosseland, 1995). Again, higher environmental concentrations of sodium, chloride and calcium seem to compensate for loss of these ions from the fish. Packer and Dunson (1970) found that trout exposed to a pH of 3.5 survived over three times longer in a solution of 150 mM sodium than trout at the same pH in a 100 M sodium solution. They also found that the trout in the 150 mM solution had normal sodium body contents at death, while those in the 100 M had lost nearly 50% of their body sodium. Milligan and Wood (1982) have proposed that the death of fish in acid waters can be traced to this ionoregulatory failure, but the final cause is circulatory, rather than ionic. They propose that a rapid drop in plasma sodium and/or chloride by more than 30% triggers a reduction in plasma volume due to water loss to the environment and tissues. This produces an increase in blood viscosity which in turn causes the arterial blood pressure to rise, which can cause circulatory failure resulting in death from hypoxia.

Acute exposure to low pH water can also affect a decrease in the blood pH of fish. Packer and Dunson (1970) found that the mean blood pH of brook trout held in a pH 8 solution was 7.39 ± 0.08 while those subjected to a pH 3 solution had a mean blood pH of 6.97 ± 0.10 at an average time to death of 1.45 ± 0.55 hours (no mortalities in control

group). Another study found that rainbow trout died when blood pH was lowered from 7.3 to 6.8 by injections of lactic acid or HCl. It would appear that blood pH must be maintained above 7.0 if the trout is to survive (Packer and Dunson, 1970). There is evidence indicating that ambient calcium concentrations control this effect on blood pH. At a low calcium level, lowering the water pH to 4.3 had no effect on the arterial pH of rainbow trout, but at high calcium levels, considerable acidosis occurred. Thus in soft water environments at realistic pH values, acidosis alone would not be a realistic cause of death to fish species (Heath, 1995).

The duration of exposure to low pH is an important factor in fish mortality. A study found that rainbow trout which had overturned after 24 hours in a pH 3.8 solution, recovered on transfer to clean water at pH 8.2. Similar results were obtained with brook trout and salmon, therefore, it would appear that salmonids do not suffer any permanent damage from exposure to acid solutions for periods of time too short to cause death (Alabaster and Lloyd, 1980).

Chronic exposure to low pH waters may last days, months and even years. Trout may respond to the prolonged exposure with a chronic depression of plasma electrolytes that can persist indefinitely or the fish may adjust to the acid water with partial or complete compensation to the stress. The character of the response depends upon the species and the presence of other ions. Another possibility may be a Darwinian response to chronic exposure, in that populations may become genetically selected for better acid tolerance (Heath, 1995).

Chronic exposure to low pH values, like acute exposure, produces an

ionoregulatory disturbance that can, albeit over a longer period of time, result in a net loss of ions from a salmonid. This loss can continue until the fish succumbs to circulatory failure and dies as mentioned previously or it is quite possible that the fish is weakened so that it may be more susceptible to disease (Alabaster and Lloyd, 1980). Another possibility is that fish may adapt to the harsh environment and survive. A study on adult rainbow trout exposed for three months to soft water with a pH of 4.8 found an initial net loss of sodium and chloride, but by 30 to 50 days into the exposure the influx and efflux rates reached a new equilibrium that maintained abnormally low but non-lethal levels of these ions. Although, there were elevated levels of plasma glucose and cortisol and a higher ammonia excretion rate, which indicates the trout were under a considerable degree of stress (Heath, 1995).

The ability of salmonids to acclimate to low pH environments is a matter of debate since there are conflicting studies. Acclimation is most likely dependent upon the strain and/or species and the environmental conditions. The rainbow trout exposed to pH 4.8 for three months mentioned above lost electrolytes more rapidly and were less tolerant of the acid when exposed to a subsequent lethal pH level than the trout that had not received a pre-exposure. This indicates that the trout were weakened by the chronic exposure and supports the theory that rainbow trout do not acclimate to low pH alone (Heath, 1995). Similar studies found no difference between the susceptibility of batches of rainbow trout acclimated to pH values of 8.4, 7.5, and 6.55 when they were exposed to lethal acid solutions and that acclimation of brook trout to pH values in the range 4-6 did not significantly increase the survival times in lethal acid solutions (Alabaster and Lloyd,

1980). In contrast, other studies found that rainbow trout exposed to soft water that the pH was gradually lowered to a value of 4 for 14 days seemed to adjust to the acid fairly well (Heath, 1995) and that brook trout raised in waters with pH values of 4.65, 4.97, and 8.07, when exposed to pH 4.0 waters, 76 percent of those raised in acid waters survived, whereas all those raised in alkaline waters died (Alabaster and Lloyd, 1980). Also, studies with inbred strains of brook trout have demonstrated that acid tolerance may be hereditary and that there may be some selection in low pH waters for strains which have an inherited resistance to these conditions (Robinson et al., 1976).

There are several other effects that low pH has on trout in general and they will be discussed in the following paragraphs.

As with most environmental stressors, low pH exposure increases the secretion of the hormone, cortisol. The elevation of cortisol levels is probably in response to ionoregulatory dysfunction since cortisol stimulates chloride cell proliferation, and sodium and potassium ATPase activity in the gills (Heath, 1995).

Another response to low pH may be an increase in mucous secretion to protect the epithelial cells in the gills. The mucous build-up can hinder the transport of oxygen across the gills and thus reduce arterial PO_2 which can affect an increase in breathing frequency and depth or result in death from hypoxia (Havas and Rosseland; 1995, Heath, 1995).

Low pH also effects the behavior of exposed trout. Superficial sense organs, such as the olfactory and taste organs, are vulnerable to acid pollution, which may disrupt their normal chemosensory functions. These disruptions can interfere with the ability to locate

food items, social interactions, schooling behavior, predator avoidance, and territoriality (Havas and Rosseland, 1995). Also, as previously mentioned, salmonids are able to sense the pH of their environment in so much as to avoid areas of low pH, which can force them to areas of higher pH and competition with a higher concentration of their own and other species (Heath, 1995).

The aforementioned effects of acid on salmonids serve to reduce their growth in low pH environments. Brook trout have been shown to grow more slowly in acid waters (pH value 4.2-5.0) over the period of a year, compared with fish kept in water with pH 5.2-6.5 (Alabaster and Lloyd, 1980). This reduced growth can result in the production of fewer eggs, which was discussed earlier.

Aluminum Toxicity

Aluminum is the third most abundant element in the earth's crust and since its solubility in water increases as pH decreases, it is leached from soils in contact with low pH water. Once mobilized into a water column, aluminum can complex with organic and inorganic species, or it may remain as free aluminum, all of which depends upon the pH of the water. At low pH values (<4.0), the majority of the aluminum is present as free aluminum (Al^{3+}) and as the pH increases, the free aluminum complexes with inorganic ligands such as hydroxide, fluoride, sulfate, etc. and organic species such as humic acids, citrate, etc. Simple monomeric (exchangeable) aluminum complexes are initially formed, and as the pH rises, higher molecular weight complexes are formed (Snoeyink and Jenkins, 1991). Toxicological studies have found that free aluminum ions and inorganic monomeric aluminum complexes are the most toxic to aquatic organisms (Gagen and

Sharpe, 1987). Therefore, acidified waters found in areas of high acid deposition serve to increase the toxic effects of aluminum.

There are several modes of aluminum toxicity. The first to be discussed has to do with the mucous layer that protects the gills. This mucous layer is made up mostly of glycoproteins and sialic acid, and at pH values around 5, the sialic acid in the mucous is primarily negatively charged. This allows positively charged aluminum species to bind to the mucous. This can irritate the gill epithelium, thus stimulating the secretion of more mucous. The excessive mucous can clog the interlamellar regions of the gills, which can hinder the uptake of oxygen and ions (Havas and Rosseland, 1995).

A second mode involves the gill boundary layer closest to the epithelium. This boundary layer maintains a circumneutral pH value even at low environmental pH. Aluminum that reaches this layer will then precipitate as aluminum hydroxide or another high molecular weight complex. The precipitate can affect the permeability of the membrane, irritate the gills, and cause gill lesions (Havas and Rosseland, 1995; Heath, 1995).

Another mode of toxicity is the ability of aluminum to bind to small electronegative species such as common biological oxygen-based functional groups (phosphates, carboxylates, carboxyls, and hydroxyls) on the gill membrane, which serves to reduce the fluidity of the membrane. Also, aluminum may substitute for the metal co-factor of transport proteins or for the transport species itself. These effects can interfere with important transcellular, diffusional and active processes, which may include the uptake of ions (Na^+ , Cl^- , Ca^{2+}), excretion of waste products (NH_4^+ , HCO_3^-), and diffusion

of respiratory gases (O_2 , CO_2). Aluminum has also been suggested to substitute for calcium in the gill epithelium, which as mentioned before, can affect membrane permeability (Havas and Rosseland, 1995). Therefore, aluminum serves to exacerbate the ionoregulatory dysfunction previously discussed. Brook trout that were exposed to pH 5.0 soft water with initial aluminum concentrations of 0.43, 0.25, 0.08, and 0.00 mg/l, were found to have median body sodium loss rates of 0.16, 0.16, 0.10, and 0.09 mg Na/(gram body weight* hour), respectively, at 16 hours of exposure and a total body sodium loss of 40.0, 36.0, 33.2, and 21.2 percent, respectively, at 24 hours of exposure. This clearly indicates that the presence of aluminum can accelerate the net sodium loss in brook trout at pH 5.0. Also, rainbow trout exposed to pH 5.2-5.4 soft water with aluminum concentrations above 0.4 mg/l experienced a 35 percent net loss of sodium in one day, whereas at aluminum concentrations below 0.1 mg/l, the rainbow trout exhibited approximate homeostasis with respect to sodium balance (Gagen and Sharpe, 1987). Once again, higher ambient concentrations of calcium and sodium can reduce the harmful effects of low pH and high aluminum concentrations (Heath, 1995).

The concentration of aluminum in the environment plays a part in its toxicity. Smith and Haines (1995) found no differences in survival or growth of brook trout exposed to pH 5.6 - 5.0 soft water for 30 days with and without the addition of 107 - 57 g/l of labile monomeric aluminum. While other toxicological studies found measurable reductions in growth and survival of brook trout at aluminum concentrations of 0.2 mg/l and a pH of 5.0 (Gagen and Sharpe, 1987). Interestingly, sublethal aluminum concentrations in acid waters seems to aid adaptation of fish to these conditions. Studies

have found that trout exposed to chronic acid stress with sublethal concentrations of aluminum showed an initial ionoregulatory dysfunction which may be greater than with acid alone, but with time, were able to show partial or complete restoration of normal plasma sodium and chloride. Also, fish acclimated to the acid and aluminum environment were better able to tolerate a subsequent challenge with a lower pH and high concentrations of aluminum (Heath, 1995).

Yet another mode of aluminum toxicity has to do with periods of high runoff, when acid, aluminum rich water can mix with alkaline water. Aluminum can then precipitate as aluminum hydroxide, which can accumulate on the gills and filtering apparatus of aquatic organisms causing acute toxicity. Since the precipitate will eventually settle, the toxicity is short-lived and limited in space (Havas and Rosseland, 1995).

Table 2-1 is a summary of the findings of this literature review.

Table 2-1. Summary of the effects of pH values on trout.

pH Range	Effects
7.0-6.0	Unlikely to be harmful unless a high runoff of acid, Al-rich water creates a mixing zone where $\text{Al}(\text{OH})_3$ precipitates causing acute toxicity.
6.0-5.0	Likely to be harmful to trout when Al concentrations exceed about 0.2 mg/l. The lower end of this range may be harmful to eggs, fry, and non-acclimated trout if calcium, sodium and chloride concentrations are low. Mechanisms: ionoregulatory dysfunction, respiratory stress.
5.0-4.5	Likely to be harmful to the eggs and fry, and to adults particularly in soft water containing low concentrations of sodium, calcium and chloride. Reduced reproduction, reduced growth, and abnormal behavioral patterns are likely in this range. Aluminum concentrations exceeding about 0.2 mg/l could increase the negative effects. Mechanisms: ionoregulatory dysfunction, respiratory stress, circulatory stress.
4.5-4.0	Likely that trout could not survive in this range for prolonged periods of time, although, natural populations of brown and brook trout have been found in this range. Reproduction in this range would be severely limited if not non-existent. Mechanisms: blood acidosis, ionoregulatory failure, respiratory failure, circulatory failure.
4.0-3.5	This range is likely to be acutely lethal to all salmonids.

Chapter III. Spatial Variability of Water Quality

One goal of the park-wide water quality monitoring is to investigate how water quality

varies spatially within the Great Smoky Mountains National Park (GRSM). This information can help to identify sensitive areas and dictate management decisions that can reduce future impacts to these areas.

Data

The following analyses utilize the chemistry data of collected samples from ninety sites within the GRSM, seven of which are high elevation springs. The data set includes samples collected from October, 1993 to November, 2001. From 1993 to 1995, samples were collected at 367 sites biannually. In 1995, the number of sites was reduced to 160 and collected on a monthly basis. In 1997, the number of sites was again reduced to 90 sites collected quarterly. Therefore, there are ninety sites with data from 1993 to the present. Table 3-1 lists sampling site locations and the watershed in which they are located. Each water sample collected was analyzed for the following water quality constituents: pH, acid neutralizing capacity (ANC), conductivity, nitrate, sulfate, chloride, sodium, potassium, and ammonium.

Methods of Analysis

A median value of each water quality constituent was calculated for every sampling site over the eight year period of record with the exception of calcium and magnesium, which have only seven sampling dates of useable data due to legacy laboratory analysis concerns. The median was used because it is more resistant to outliers

Table 3-1. Sample site descriptions and locations.

Sample site	Site description	Watershed
1	Indian Camp at Old Settlers	Indian Camp Creek
3	Cosby Creek at boundary	Cosby Creek
4	Lower Rock Creek	Cosby Creek
13	Little River at boundary	EPLR
14	Little River above Y	EPLR
20	Little River at Metcalf Bottoms	EPLR
23	Lower Middle Prong Little River	MPLR
24	Lower West Prong Little River	WPLR
30	West Prong Little Pigeon at headquarters	WPLPR
34	Little River at Milsap Site	EPLR
43	Porters Creek at log bridge	MPLPR
45	Shutts Prong	MPLPR
46	Porters Creek above Shutts Prong	MPLPR
47	Lower Cannon Creek	MPLPR
49	Porters Creek at bridge to Ramsay	MPLPR
50	Middle Prong Little Pigeon below Porters	MPLPR
52	Middle Prong Little Pigeon at boundary	MPLPR
66	West Prong Little Pigeon at Chimneys picnic area	WPLPR
71	Road Prong above barrier cascade	WPLPR
73	Walker Camp Prong above Road Prong	WPLPR
74	Walker Camp Prong above Alum Cave Creek	WPLPR
103	Otter Creek	Indian Camp Creek
104	Copperhead Branch	Indian Camp Creek
106	Upper Indian Camp Prong	Indian Camp Creek
107	Indian Camp below Albright Grove	Indian Camp Creek
114	Cosby Creek at log bridge	Cosby Creek
115	Upper Cosby Creek	Cosby Creek
127	Pretty Hollow Creek above Palmer Creek	Cataloochee Creek
137	Upper Rock Creek	Cosby Creek
138	Inadu Creek	Cosby Creek
142	Beech Creek above Lost Bottom Creek	Cataloochee Creek
143	Lost Bottom Creek	Cataloochee Creek
144	Palmer Creek above Pretty Hollow Creek	Cataloochee Creek
147	Lower Cataloochee Creek	Cataloochee Creek
148	Lower Little Cataloochee Creek	Cataloochee Creek
149	Middle Cataloochee Creek at bridge	Cataloochee Creek
150	Cataloochee Creek below Caldwell Fork	Cataloochee Creek
156	Abrams Creek at ranger station	Abrams Creek
173	Mill Creek above Abrams Creek	Abrams Creek
174	Abrams Creek below Cades Cove	Abrams Creek
183	Spring at Russell Field shelter	Abrams Creek
184	Left Fork Anthony Creek at campsite 10	Abrams Creek
186	Anthony Creek above picnic area	Abrams Creek
190	Thunderhead Prong at trail crossing	MPLR

Note: Abbreviations in the table are as follows: EPLR, East Prong Little River; MPLR, Middle Prong Little River; WPLR, West Prong Little River; MPLPR, Middle Prong Little Pigeon River; WPLPR, West Prong Little Pigeon River.

Table 3-1 (cont.)

Sample site	Site description	Watershed
191	Sams Creek	MPLR
192	Starkey Creek	MPLR
193	Middle Prong Little River at old trailhead	MPLR
194	Middle Prong Little River above Tremont	MPLR
195	Spring at Spence Field shelter	Eagle Creek
200	Anthony Creek above campsite 9	Abrams Creek
201	Anthony Creek below Spence Field	Abrams Creek
209	Lost Creek	EPLR
210	Little River above Fish Camp Prong	EPLR
213	Goshen Prong above Fish Camp Prong	EPLR
214	Silers Creek	EPLR
215	Ashe Camp Prong	EPLR
218	Spring at Silers Bald Shelter	EPLR
219	Double Springs Gap shelter (North Carolina side)	Forney Creek
220	Double Springs Gap shelter (Tennessee side)	EPLR
221	Hazel Creek above cascades	Hazel Creek
233	Walker Camp Prong above Alum Cave	WPLPR
234	Upper Road Prong	WPLPR
237	Walker Camp Prong at last bridge	WPLPR
251	Beech Flats above US 441 loop	Oconaluftee River
252	Beech Flats below roadcut	Oconaluftee River
253	Beech Flats above roadcut	Oconaluftee River
266	Oconaluftee River at visitors center	Oconaluftee River
268	Oconaluftee River below Smokemont	Oconaluftee River
290	Bear Branch at campsite 42	Cataloochee Creek
291	Bunches Creek above Balsam Mountain Road	Bunches Creek
293	Rough Fork at Caldwell House	Cataloochee Creek
310	Bone Valley Creek	Hazel Creek
311	Hazel Creek below Haw Gap Creek	Hazel Creek
336	Flat Creek above falls	Bunches Creek
337	Bunches Creek at Flat Creek Trail	Bunches Creek
472	Sams Creek above Thunderhead Prong	MPLR
473	West Prong Little Pigeon River across from Bearpen Prong	WPLPR
474	Little River below Husky Branch at resting bench	EPLR
475	Fish Camp Prong at angled barrier below War Branch	EPLR
479	Hazel Creek at campsite 86	Hazel Creek
480	Haw Gap Creek at bridge near campsite 84	Hazel Creek
481	Little Fork above Sugar Fork Trail	Hazel Creek
482	Sugar Fork above Little Fork	Hazel Creek
483	Sugar Fork above Haw Gap Creek	Hazel Creek
484	Hazel Creek at Cold Spring Gap Trail	Hazel Creek
485	Walker Creek above Hazel Creek Trail	Hazel Creek
488	Mill Creek at Pumphouse on Forge Creek Road	Abrams Creek
489	Abrams Creek 300 meters below trailhead bridge	Abrams Creek
492	Camel Hump Creek off Low Gap Trail	Cosby Creek
493	Palmer Creek at Davidson Branch Trail	Cataloochee Creek

than the mean and probably better reflects typical conditions (Helsel and Hirsch, 1992). The median pH values were used to identify the number of sites that could be of concern based on criteria presented in the literature review in chapter 2. Also, descriptive statistics and frequency analysis were used to show how the median pH values vary greatly within the GRSM.

Simple linear regression was performed on the median values with respect to sample site elevation in order to determine if statistically significant trends exist ($p < 0.05$). Scatter plots were used to graphically represent the data.

Box plots were also used to show the variability in the median constituent values over elevation ranges of 500 feet (152m). The box portion of the box plot represents the interquartile range within which fifty percent of the values are contained. The lower end of the box is the 25th percentile and the upper is the 75th percentile. The whiskers extending above and below the box represent the 90th and 10th percentiles, respectively. The circles represent mild outliers, which are within 1.5 times the interquartile range from the 25th and 75th percentiles. Asterisks represent extreme outliers, which are greater than 3 times the interquartile range away from the 25th and 75th percentiles.

Results

Table 3-2 lists the median water quality constituents for each sampling site. Ammonium is excluded from this table because the median value was below detection limits for every sampling site. Table 3-3 contains descriptive statistics for each water quality constituent. Figure 3-1 presents a histogram of the median pH values.

Table 3-2. Median water quality values

Site ID	Elev. (ft)	Elev. (m)	pH	ANC (µeq/L)	Cond. (µS/cm)	Cl (µeq/L)	NO3 (µeq/L)	SO4 (µeq/L)	Na (µeq/L)	K (µeq/L)	Mg (µeq/L)	Ca (µeq/L)
1	2200	671	6.24	35.30	15.41	13.80	24.54	46.90	34.79	11.74	20.25	65.43
3	1675	511	6.50	73.20	15.55	12.89	16.91	34.90	47.21	10.02	29.71	63.80
4	2080	634	6.33	60.03	13.93	12.28	6.03	24.45	46.60	10.92	23.37	54.50
13	1100	335	6.61	110.07	17.28	14.76	6.44	34.83	41.20	12.35	35.56	74.55
14	1140	347	6.61	102.16	17.05	14.61	6.59	34.64	41.46	13.50	32.02	74.20
20	1700	518	6.50	85.10	15.40	13.26	8.72	33.61	39.36	12.20	26.42	65.60
23	1150	351	6.56	98.32	16.02	15.47	7.85	31.37	36.45	10.93	35.76	61.18
24	1150	351	6.69	145.34	22.50	15.75	5.40	42.35	53.95	12.89	48.48	101.85
30	1430	436	6.44	59.52	19.75	16.84	25.06	63.26	34.81	9.16	39.51	79.00
34	1960	597	6.43	64.26	14.26	18.10	10.63	32.66	35.86	11.88	24.24	60.08
43	2340	713	5.89	10.64	15.86	13.34	24.26	62.80	25.76	6.02	30.86	48.75
45	3200	975	5.57	3.73	18.98	15.40	31.60	86.49	22.30	4.46	41.15	52.25
46	2750	838	5.77	5.39	16.75	14.21	28.90	72.43	25.71	4.39	36.05	50.20
47	2400	732	5.92	11.05	11.75	13.39	20.46	40.90	24.83	8.89	17.12	35.55
49	1670	509	6.26	39.33	15.86	13.61	17.15	50.19	32.99	7.39	33.50	74.50
50	1665	507	6.33	38.67	14.52	15.36	17.32	46.93	34.76	8.66	24.69	55.50
52	1350	411	6.39	51.71	15.53	14.17	16.06	47.72	37.13	8.28	27.41	61.75
66	2680	817	6.27	33.97	19.08	14.97	32.16	69.52	25.47	6.58	39.18	76.75
71	3400	1036	6.19	26.05	15.74	14.86	31.91	44.77	28.03	8.31	28.48	68.05
73	3360	1024	6.33	31.35	19.90	16.14	33.27	78.45	23.31	5.06	43.87	77.23
74	3820	1164	6.42	53.31	23.80	15.51	34.22	89.89	24.57	4.74	55.14	122.00
103	4330	1320	5.60	2.16	19.61	14.41	48.72	67.23	28.81	10.83	21.07	77.20
104	4200	1280	5.68	4.01	18.08	14.01	49.88	55.80	28.09	12.38	20.58	71.65
106	3840	1170	6.00	16.27	17.41	14.73	41.12	58.11	27.93	13.17	21.98	80.50
107	3040	927	6.04	19.59	16.06	11.91	34.28	53.39	27.47	11.46	19.67	68.80
114	2510	765	6.28	36.71	16.97	15.53	39.11	44.76	36.44	9.21	33.58	64.15
115	3840	1170	6.19	37.12	15.95	16.91	28.79	48.08	32.69	7.95	34.90	63.23
127	2980	908	6.40	46.53	11.20	15.64	14.58	19.40	38.31	11.18	19.18	36.90
137	2750	838	5.88	11.80	14.53	13.67	31.31	51.77	30.37	8.37	27.24	54.10
138	3470	1058	5.53	3.01	13.73	15.19	34.98	37.51	27.99	8.92	18.60	42.60
142	3300	1006	6.46	56.72	10.92	13.47	7.37	15.16	36.05	11.91	17.78	38.40
143	3280	1000	6.41	48.53	10.69	14.40	8.12	20.82	38.86	10.85	16.46	34.55
144	2990	911	6.44	54.60	10.68	13.62	6.90	17.53	38.47	11.64	17.61	37.45
147	2460	750	6.60	86.11	14.63	14.37	7.99	21.33	49.42	14.28	26.58	52.55
148	2475	754	6.67	127.92	16.76	14.95	4.30	19.36	69.63	15.72	31.03	65.60
149	2550	777	6.55	80.43	13.81	14.73	8.23	21.27	50.21	14.65	26.83	49.65
150	2620	799	6.53	79.18	13.39	15.49	9.10	20.61	49.38	13.64	25.43	50.50
156	1110	338	7.24	506.60	48.85	20.81	3.01	43.45	54.70	16.32	117.70	226.65
173	1715	523	6.66	102.39	16.90	17.31	5.33	26.23	45.12	11.91	37.20	62.50
174	1715	523	7.40	1096.36	103.50	22.01	12.26	51.37	55.48	16.18	226.34	1067.50
183	4280	1305	5.70	36.69	9.10	14.53	5.04	8.69	30.70	6.25	10.16	16.18
184	2830	863	6.20	31.25	12.89	19.01	26.00	27.52	38.97	11.24	17.53	46.40
186	1965	599	6.36	47.63	13.08	16.54	17.45	29.04	41.04	11.36	19.59	46.00
190	2120	646	6.24	28.92	11.67	13.85	16.15	31.24	31.96	8.31	17.78	39.65

Table 3-2 (cont.)

Site ID	Elev. (ft)	Elev. (m)	pH	ANC (µeq/L)	Cond. (µS/cm)	Cl (µeq/L)	NO3 (µeq/L)	SO4 (µeq/L)	Na (µeq/L)	K (µeq/L)	Mg (µeq/L)	Ca (µeq/L)
191	3200	975	6.12	20.48	10.52	15.49	19.50	26.45	29.58	9.16	15.06	35.25
192	3200	975	6.11	22.26	12.66	13.55	22.18	41.44	25.92	6.57	23.46	50.50
193	1920	585	6.39	53.67	11.40	14.69	7.58	23.65	35.80	9.85	20.58	38.70
194	1700	518	6.33	45.18	11.40	15.80	10.18	28.25	34.26	9.28	21.15	41.40
195	4810	1466	5.77	29.11	7.55	14.94	3.40	8.23	24.89	5.91	9.38	17.55
200	3320	1012	6.13	27.44	12.43	17.38	26.35	26.90	33.86	10.75	16.30	42.65
201	4800	1463	5.73	34.37	10.69	12.64	12.64	15.18	27.33	9.60	13.09	32.50
209	2700	823	6.24	32.99	9.86	13.91	6.07	24.55	33.13	9.68	16.21	28.50
210	2740	835	6.39	49.75	14.10	12.52	13.88	39.47	32.34	10.47	22.39	61.58
213	3340	1018	6.11	21.01	11.18	13.77	20.32	29.48	28.72	8.31	19.59	34.88
214	3440	1049	6.29	37.81	10.99	15.99	14.00	22.90	32.35	9.96	17.86	34.10
215	3380	1030	6.36	49.68	13.32	15.38	12.35	34.54	36.69	9.33	25.51	50.35
218	5440	1658	5.04	2.44	21.00	17.34	49.96	57.93	26.69	13.38	25.84	43.80
219	5510	1679	4.90	-1.20	23.85	15.60	79.58	59.80	25.92	12.78	21.32	52.78
220	5500	1676	5.30	3.40	16.60	12.39	57.40	30.95	26.05	11.80	20.74	50.80
221	4000	1219	6.18	26.30	10.29	15.23	24.56	16.56	32.17	9.05	16.91	29.23
233	4255	1297	6.13	30.75	22.95	16.94	34.24	106.97	23.70	4.24	54.73	102.00
234	5000	1524	5.88	17.40	15.60	16.79	57.16	27.54	33.99	6.09	27.20	48.88
237	4520	1378	4.82	-14.26	19.73	13.41	33.83	70.45	17.83	3.23	32.92	47.85
251	4010	1222	6.10	21.54	31.00	17.88	37.44	170.37	43.87	10.56	81.07	118.40
252	4680	1426	5.01	-2.84	42.30	17.45	54.20	305.02	49.05	12.04	71.60	109.60
253	4760	1451	6.43	83.44	23.50	19.23	56.65	41.36	54.63	9.18	46.50	96.00
266	2015	614	6.52	71.25	13.68	15.68	5.69	25.74	43.67	12.20	23.37	46.50
268	2185	666	6.43	64.98	13.12	14.60	8.44	28.92	42.08	11.13	25.19	49.85
290	5540	1689	5.05	-5.40	16.15	15.78	51.49	20.97	29.60	7.76		
291	5260	1603	6.10	25.19	12.55	16.13	35.57	23.44	36.42	10.29	19.34	43.30
293	2755	840	6.56	84.01	16.05	15.79	18.01	23.98	52.97	13.66	31.60	57.85
310	2240	683	6.49	71.41	11.88	15.49	3.91	21.19	40.60	10.23	25.43	47.05
311	2155	657	6.48	63.75	11.80	14.51	4.59	17.26	40.80	10.85	21.81	39.95
336	4760	1451	6.36	47.52	11.25	16.44	25.26	9.07	39.35	12.33	20.25	34.35
337	4740	1445	6.27	42.03	11.90	15.53	26.54	16.77	37.18	10.43	21.15	36.05
472	2200	671	6.17	29.40	11.60	15.46	15.08	32.70	32.34	8.52	21.89	43.10
473	3630	1106	6.18	27.95	20.30	17.31	32.04	81.55	23.28	5.47	45.88	86.00
474	2400	732	6.30	51.92	13.01	14.68	12.27	32.50	35.20	10.72	20.99	49.00
475	2950	899	6.31	35.32	11.50	17.33	15.75	28.68	31.85	10.45	20.49	40.50
479	1740	530	6.46	68.91	12.20	14.80	3.68	17.96	41.33	11.53	21.98	41.15
480	2185	666	6.51	80.47	13.35	14.32	2.14	21.36	45.93	12.24	27.98	45.95
481	2540	774	6.49	88.19	16.95	14.13	0.00	49.89	42.79	12.92	45.27	53.00
482	2540	774	6.49	84.71	13.14	14.92	2.41	21.14	45.37	11.40	34.65	44.00
483	2320	707	6.51	87.59	14.25	15.16	0.00	28.86	47.65	13.30	33.25	47.63
484	2475	754	6.41	53.11	10.50	15.35	7.16	16.52	36.30	10.12	18.85	35.95
485	2860	872	6.49	69.54	11.02	14.41	2.54	14.41	38.54	10.92	21.73	39.15
488	1790	546	6.40	44.27	11.50	16.92	9.66	22.85	39.25	10.21	19.42	37.55
489	1710	521	7.43	927.31	92.00	23.36	10.66	45.94	56.82	15.59	176.54	766.00
492	2730	832	6.15	28.05	16.70	15.45	45.53	41.33	34.27	8.39	35.06	60.73
493	2840	866	6.48	64.68	12.10	14.45	7.96	17.80	45.15	11.99	18.93	42.20
Shaded cells are high elevation springs.												

Table 3-3. Descriptive statistics of median water quality values

Water Quality Parameter	N	Minimum	Maximum	Mean	Std. Deviation
Median pH	90	4.82	7.43	6.22	0.46
Median ANC (eq/L)	90	-14.26	1096.36	72.18	154.22
Median Conductivity (S/cm)	90	7.55	103.50	17.41	13.61
Median Chloride (eq/L)	90	11.91	23.36	15.36	1.93
Median Nitrate (eq/L)	90	0.00	79.58	20.73	16.49
Median Sulfate (eq/L)	90	8.23	305.02	41.42	37.13
Median Sodium (eq/L)	90	17.83	69.63	36.58	9.47
Median Potassium (eq/L)	90	3.23	16.32	10.22	2.80
Median Magnesium (eq/L)	89	9.38	226.34	32.45	30.21
Median Calcium (eq/L)	89	16.18	1067.50	76.06	133.01

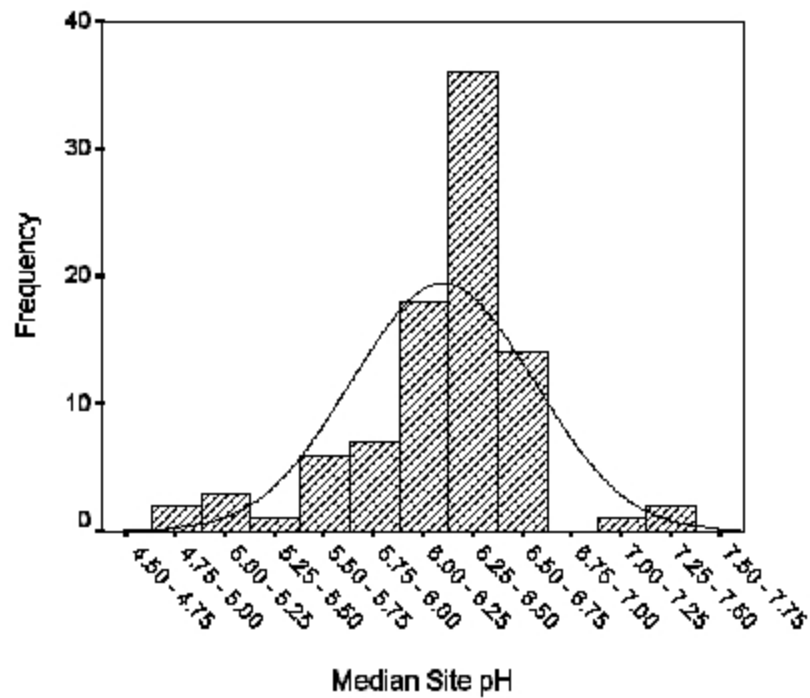


Figure 3-1. Histogram of median site pH values and calculated normal distribution

Figures 3-2, 3-4, 3-7, 3-9, 3-11, 3-13, 3-15, 3-17, 3-19, 3-20 and 3-22 are box plots, which show the variability in pH, ANC, conductivity, nitrate, sulfate, chloride, sodium, potassium, ammonium, magnesium and calcium, respectively versus elevation.

Scatter plots of the median water quality constituent values versus sample site elevation are presented in figures 3-3, 3-5, 3-6, 3-8, 3-10, 3-12, 3-14, 3-16, 3-18, 3-21, 3-23, 3-24, and 3-25. Regression analyses were performed on these data. Regression equations are included in the plot if the model is significant at an alpha level of 0.05 and the r-square is greater than 0.25. Scatter plots for ANC, calcium and magnesium are included with and without the Cades Cove sample sites, because these sites have much larger values for these constituents due to geology and may mask general elevation trends.

Discussion of Results

The results for each water quality parameter will be discussed in the following order: pH, ANC, conductivity, nitrate, sulfate, chloride, sodium, potassium, ammonium, magnesium, and calcium.

pH

Stream water pH is one of the most important water quality parameters measured in the GRSM. It is a good indicator of the stream health, which includes the stream's ability to sustain aquatic life. Currently, only three sampling sites within the GRSM have median pH values above 7.0. These sites are located on Abrams Creek, which is characterized by limestone geology. The majority (68 of 90 or 75.6 percent) of the sampling sites have median pH values within the 6.0 to 7.0 range. Previous work by

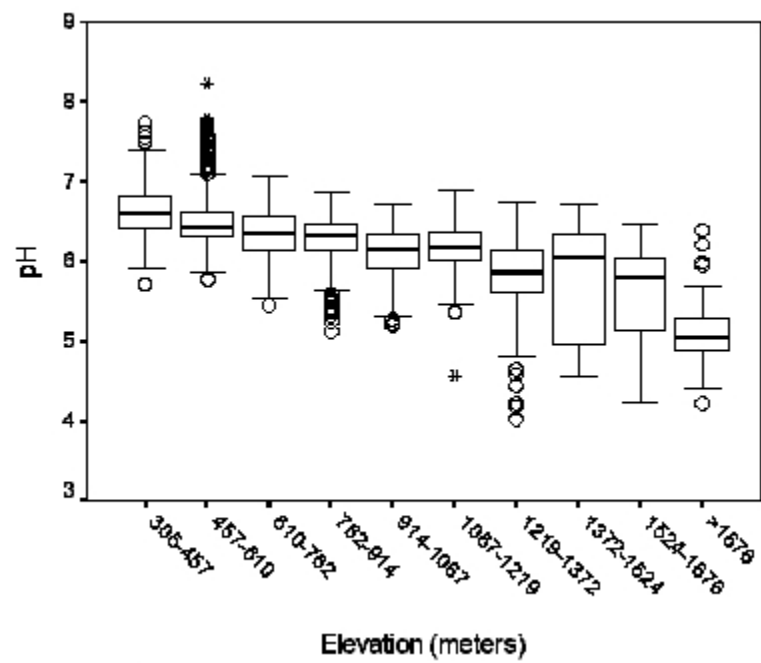


Figure 3-2. Variability of pH in sampled GRSM streams

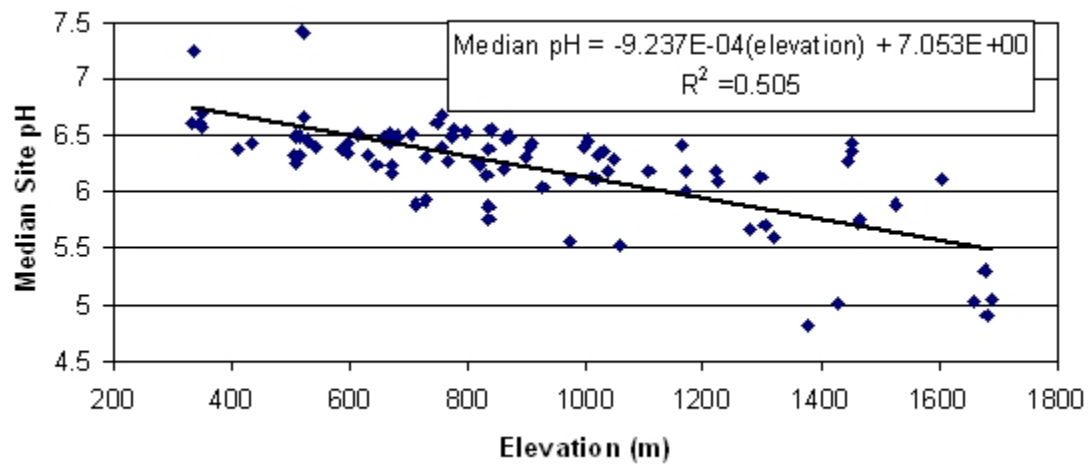


Figure 3-3. Regression analysis of median pH in sampled GRSM streams

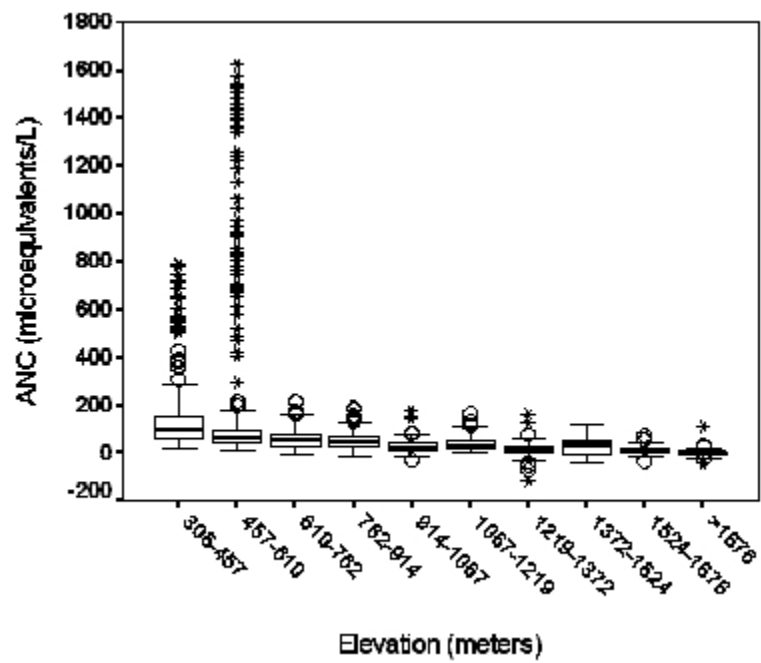


Figure 3-4. Variability of acid neutralizing capacity in sampled GRSM streams

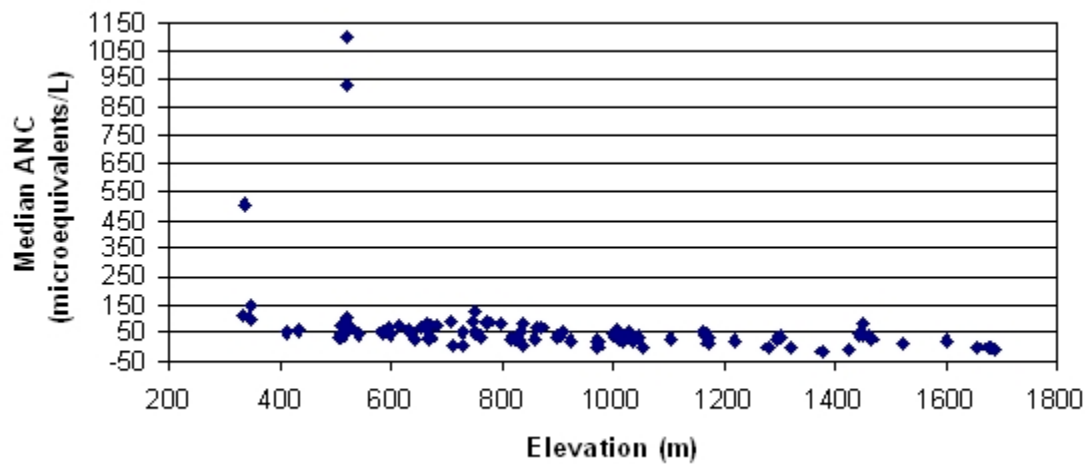


Figure 3-5. Scatter plot of median acid neutralizing capacity in sampled GRSM streams

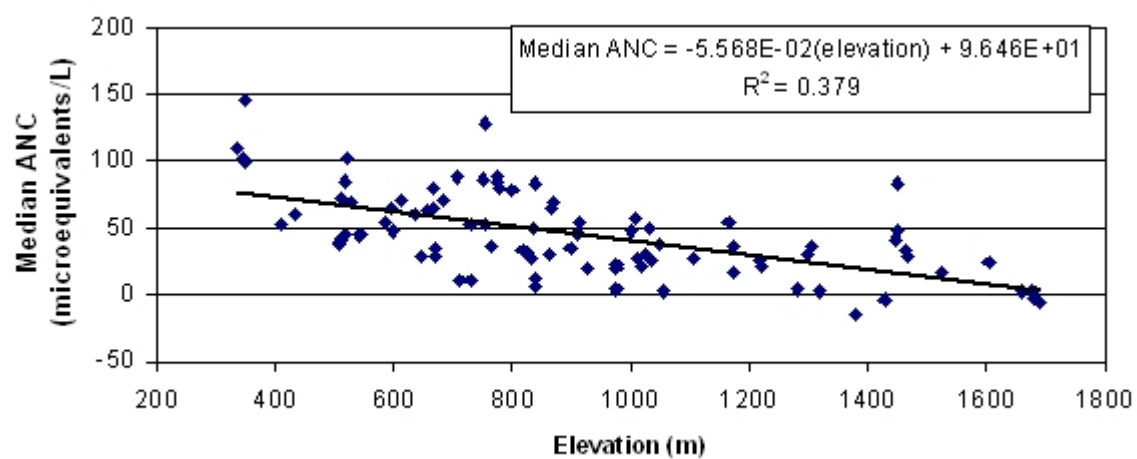


Figure 3-6. Scatter plot of median acid neutralizing capacity in sampled GRSM streams without Cades Cove sites

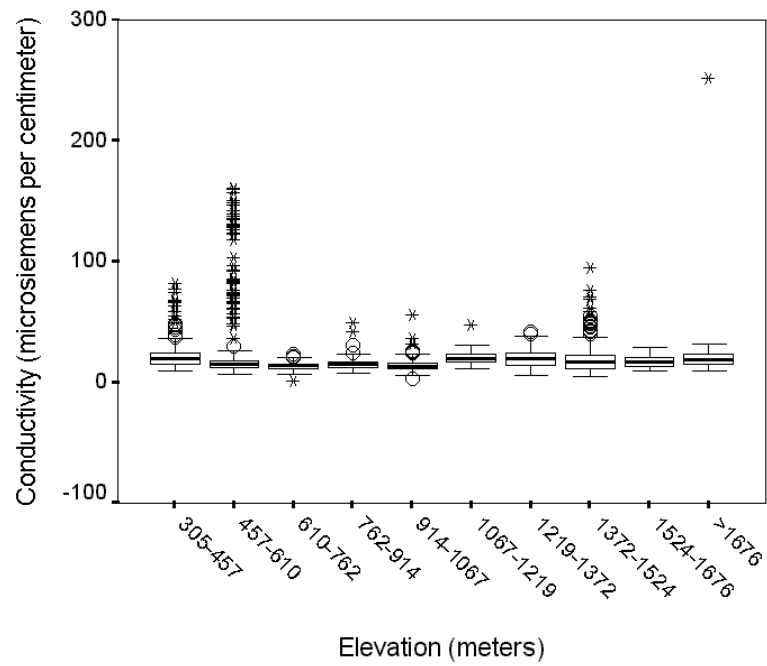


Figure 3-7. Variability of conductivity in sampled GRSM streams

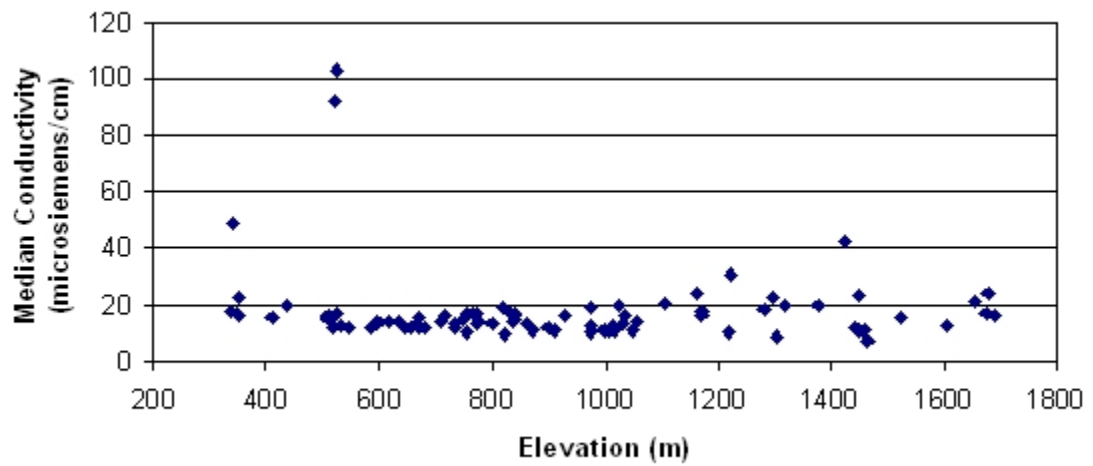


Figure 3-8. Scatter plot of median conductivity in sampled GRSM streams

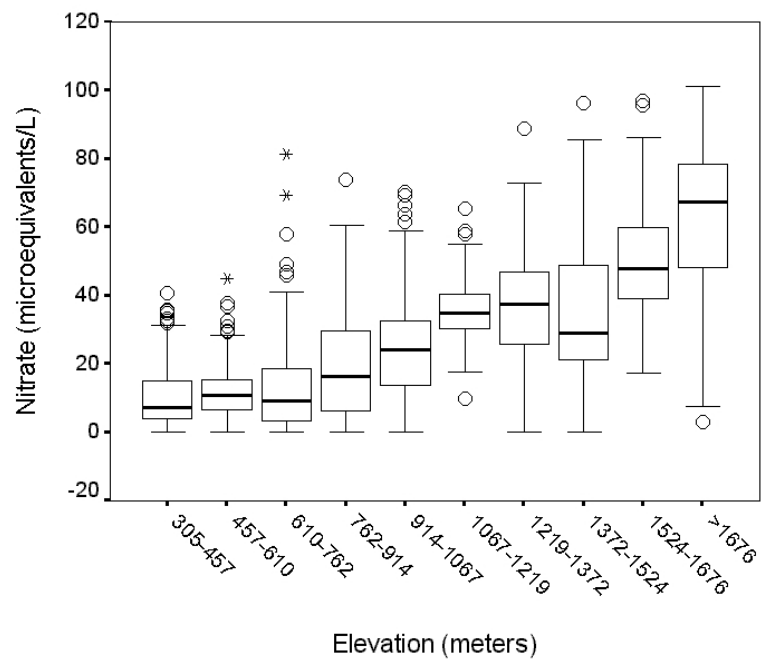


Figure 3-9. Variability of nitrate in sampled GRSM streams

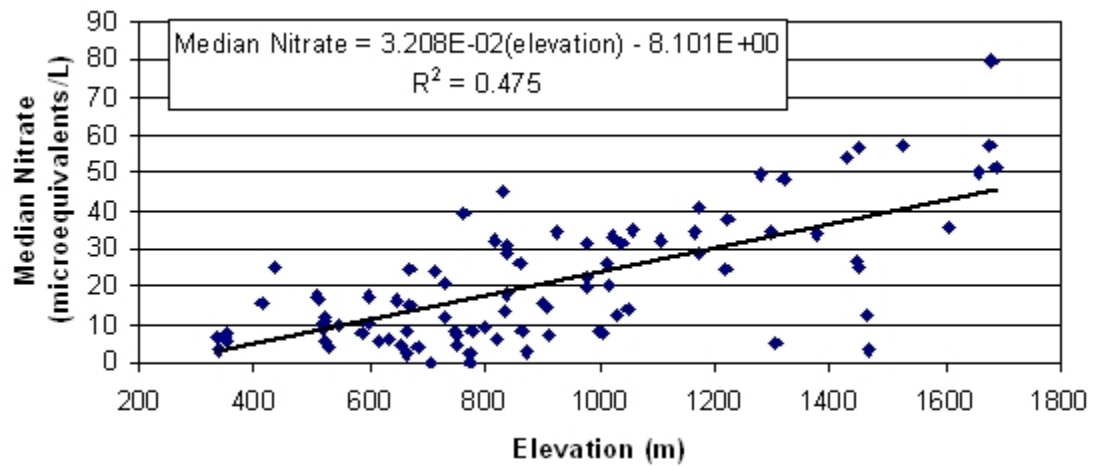


Figure 3-10. Scatter plot of median nitrate in sampled GRSM streams

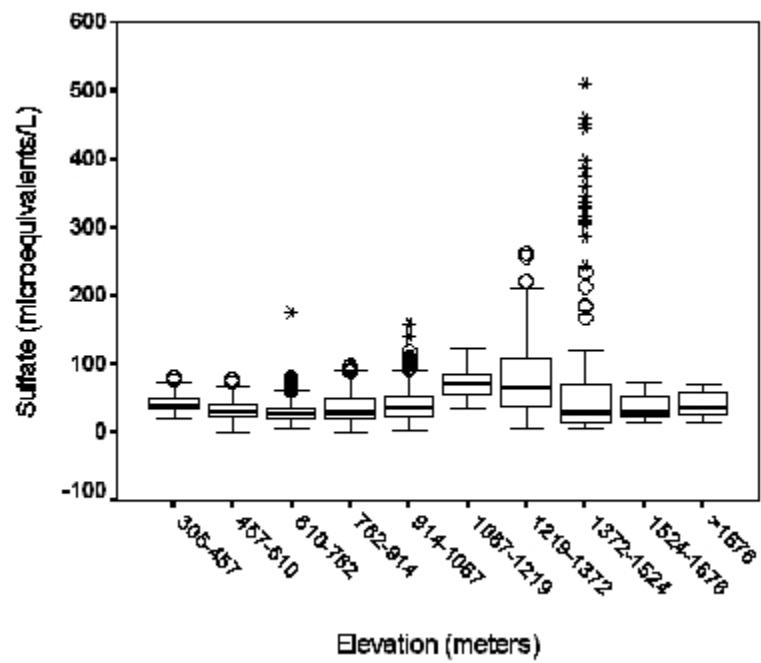


Figure 3-11. Variability of sulfate in sampled GRSM streams

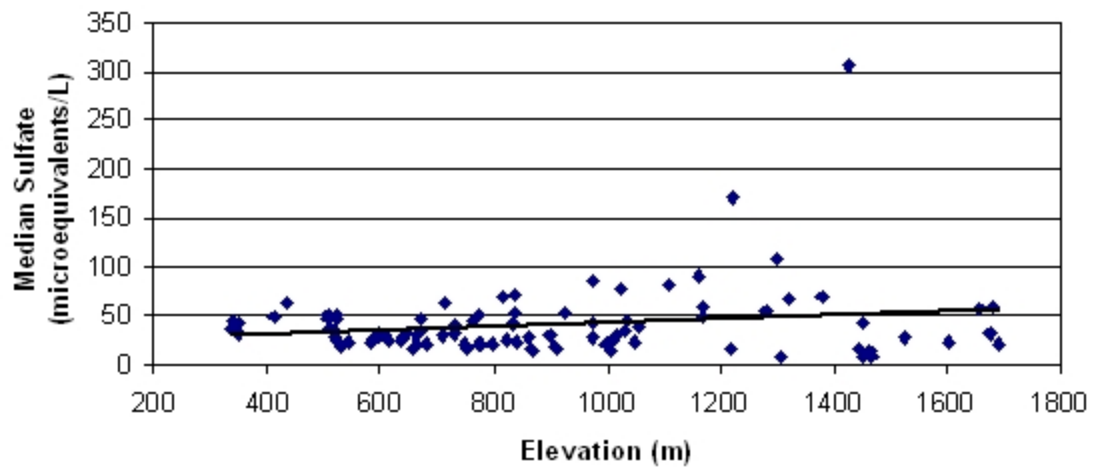


Figure 3-12. Scatter plot of median sulfate in sampled GRSM streams

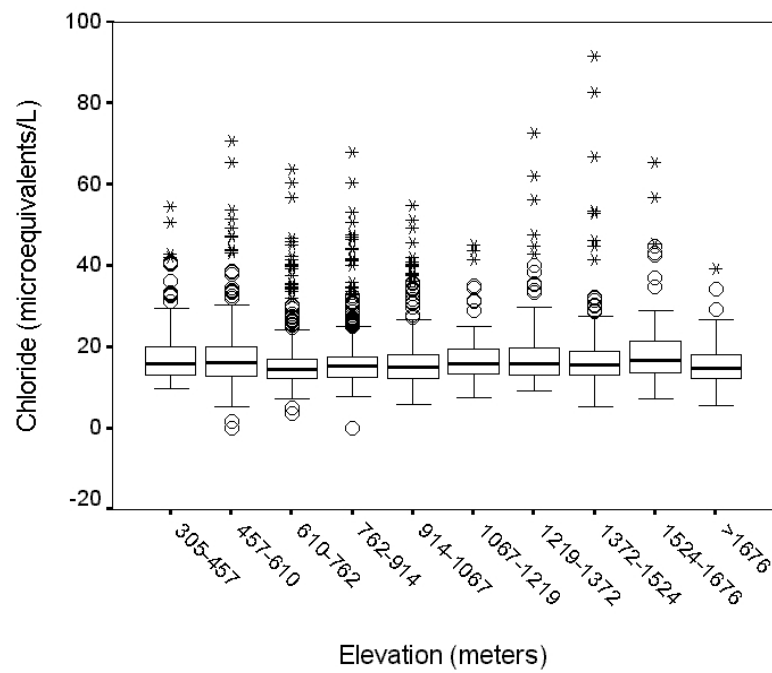


Figure 3-13. Variability of chloride in sampled GRSM streams

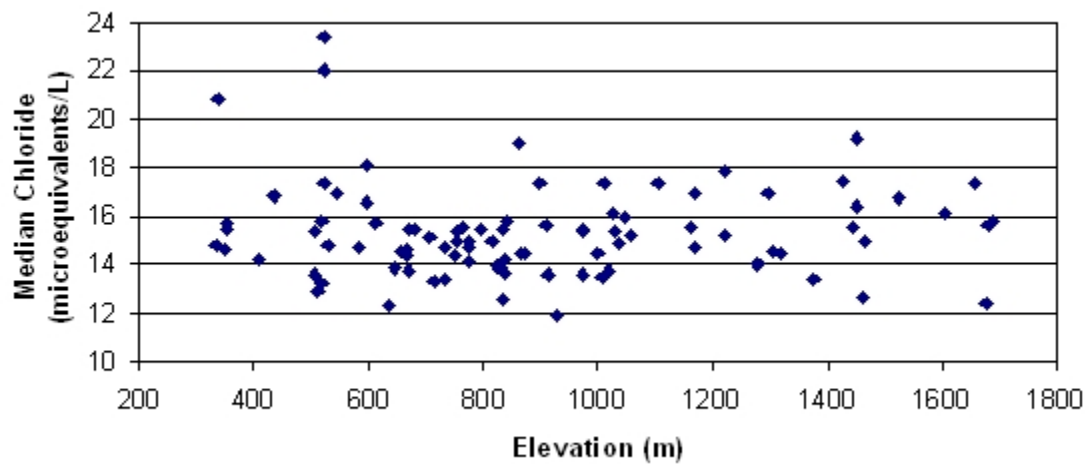


Figure 3-14. Scatter plot of median chloride in sampled GRSM streams

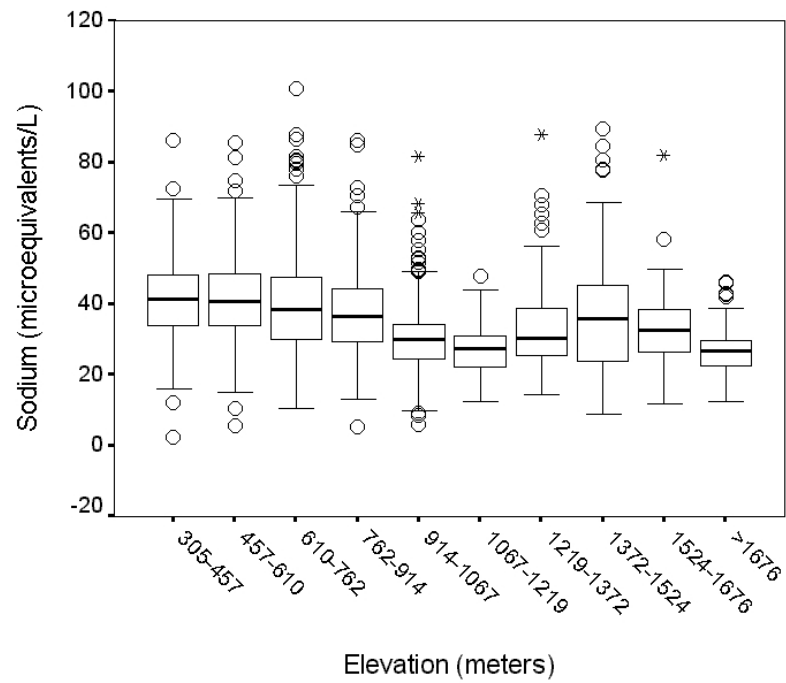


Figure 3-15. Variability of sodium in sampled GRSM streams

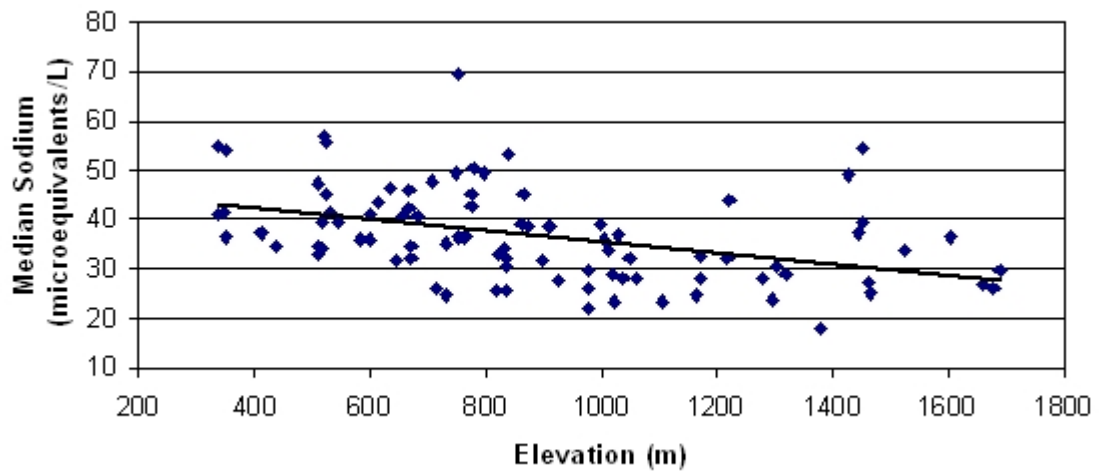


Figure 3-16. Scatter plot of median sodium in sampled GRSM streams

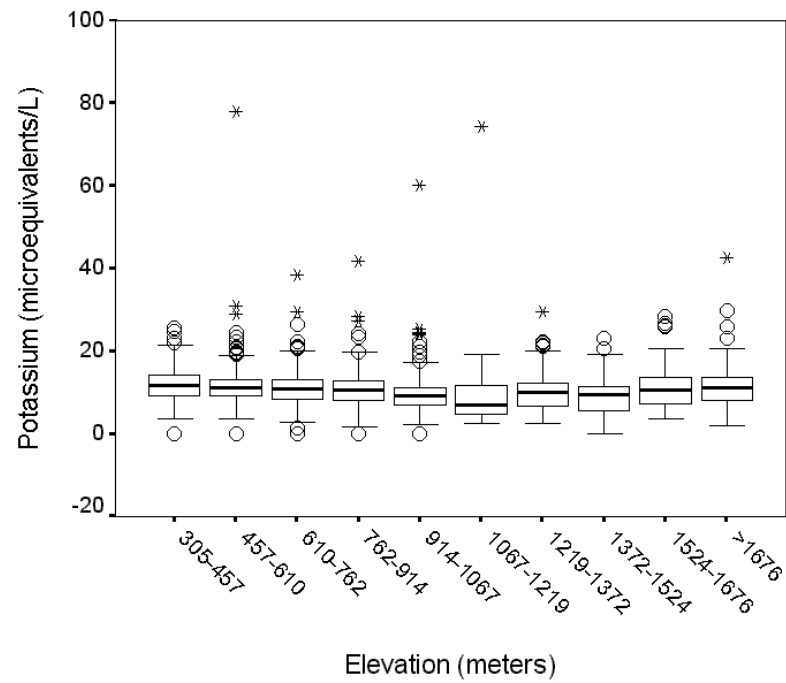


Figure 3-17. Variability of potassium in sampled GRSM streams

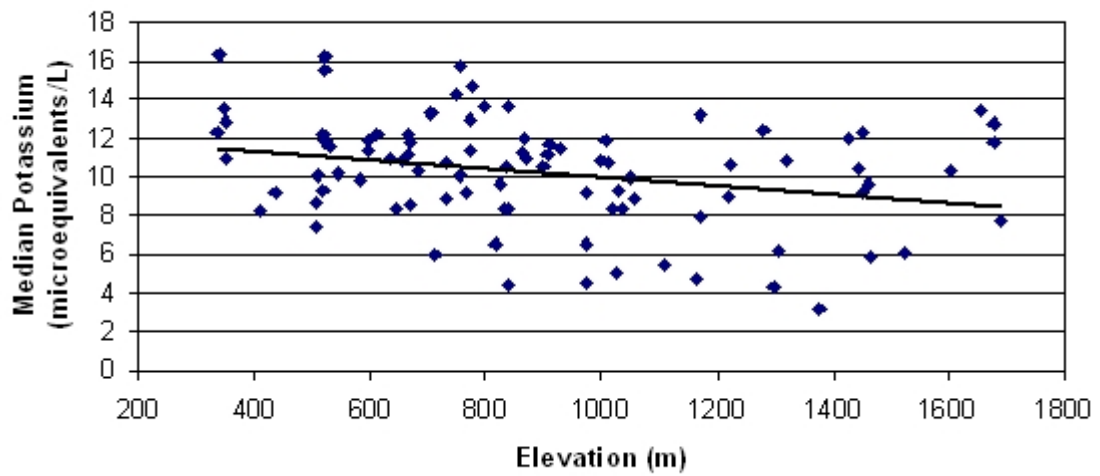


Figure 3-18. Scatter plot of median potassium in sampled GRSM streams

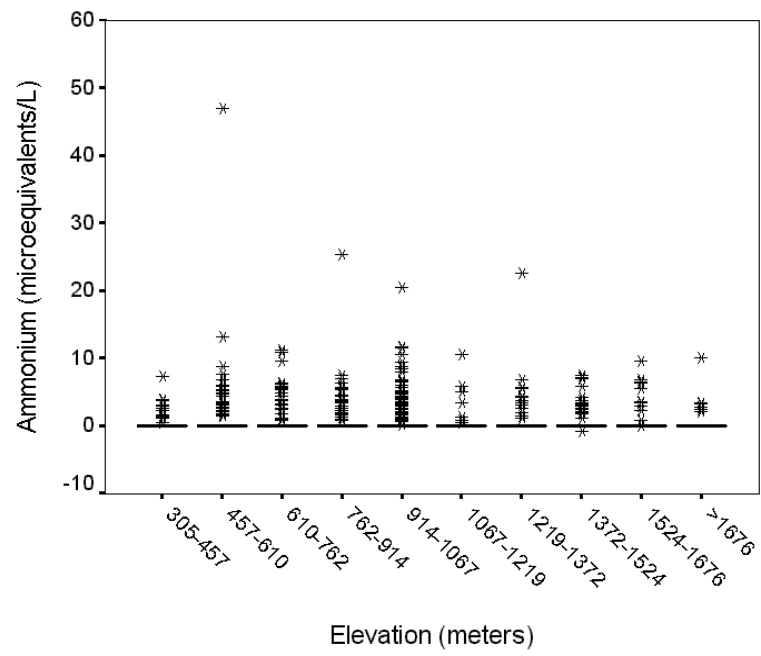


Figure 3-19. Variability of ammonium in sampled GRSM streams

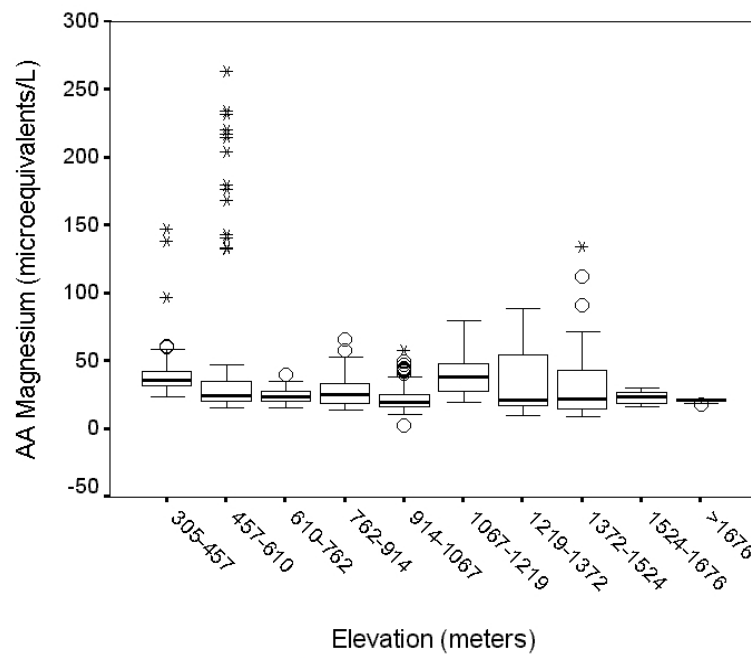


Figure 3-20. Variability of magnesium in sampled GRSM streams

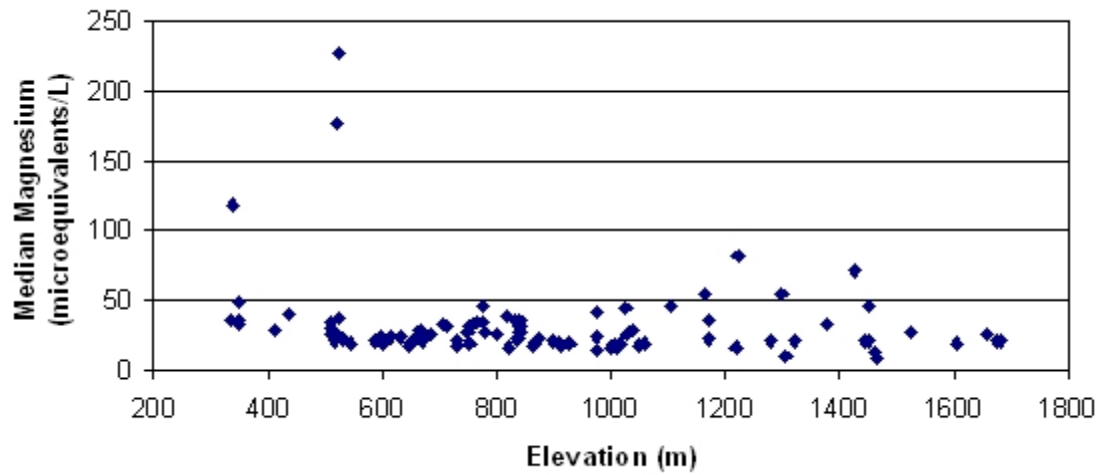


Figure 3-21. Scatter plot of median magnesium in sampled GRSM streams

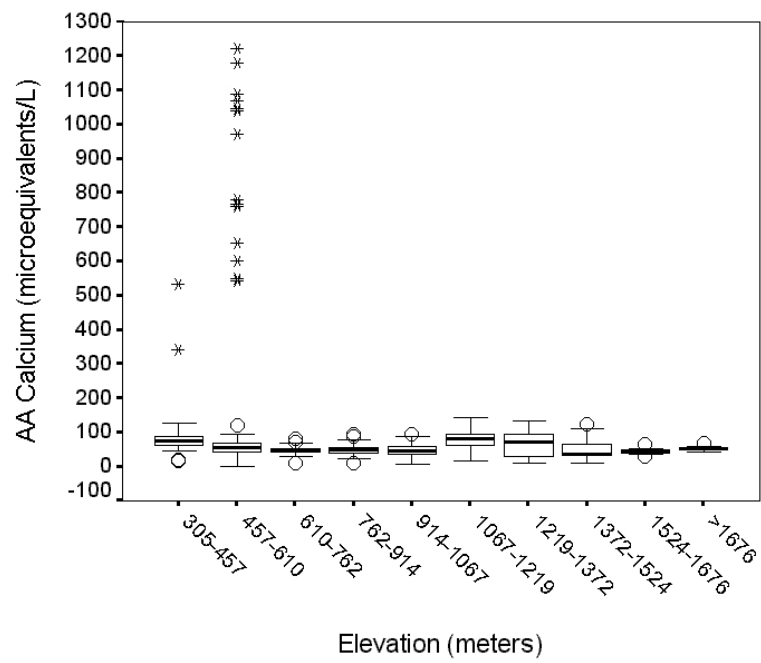


Figure 3-22. Variability of calcium in sampled GRSM streams

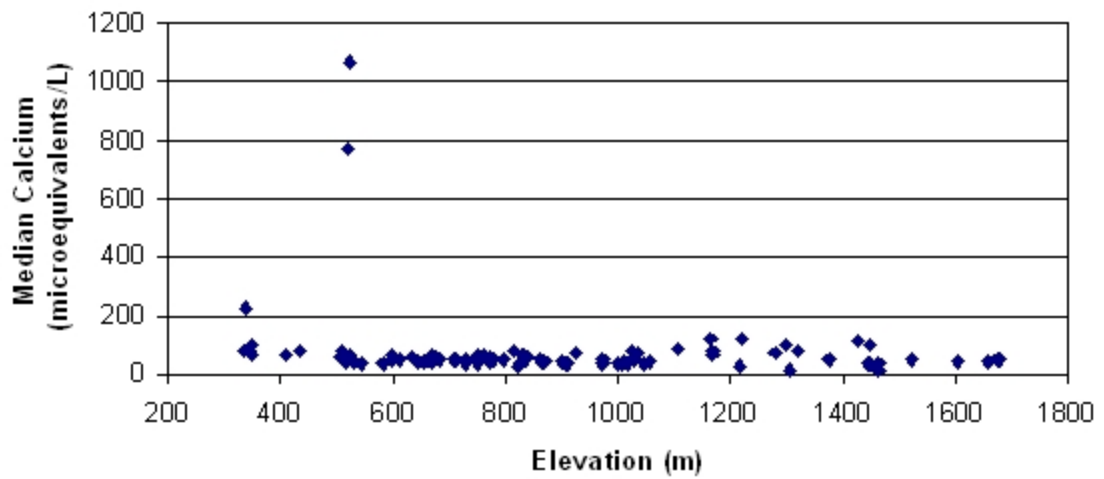


Figure 3-23. Scatter plot of median calcium in sampled GRSM streams

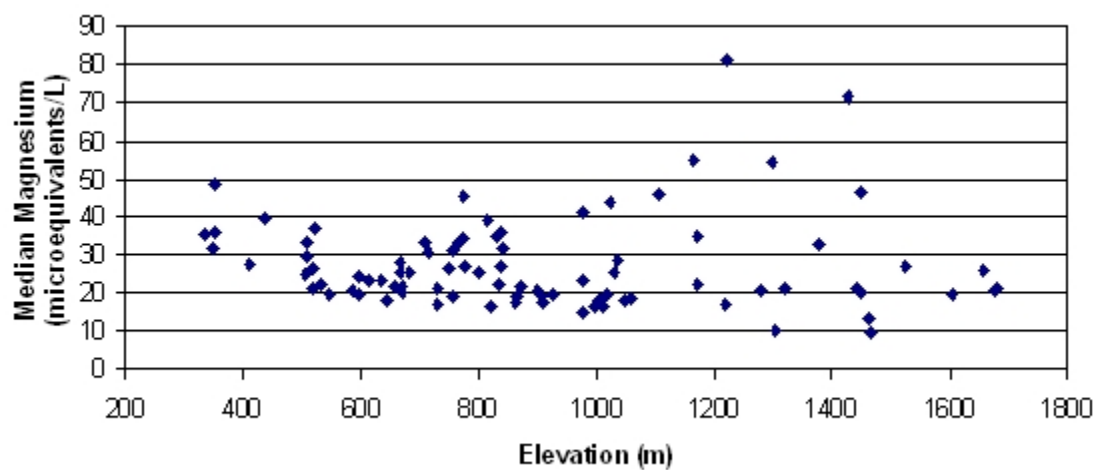


Figure 3-24. Scatter plot of median magnesium in sampled GRSM streams without Cades Cove sites

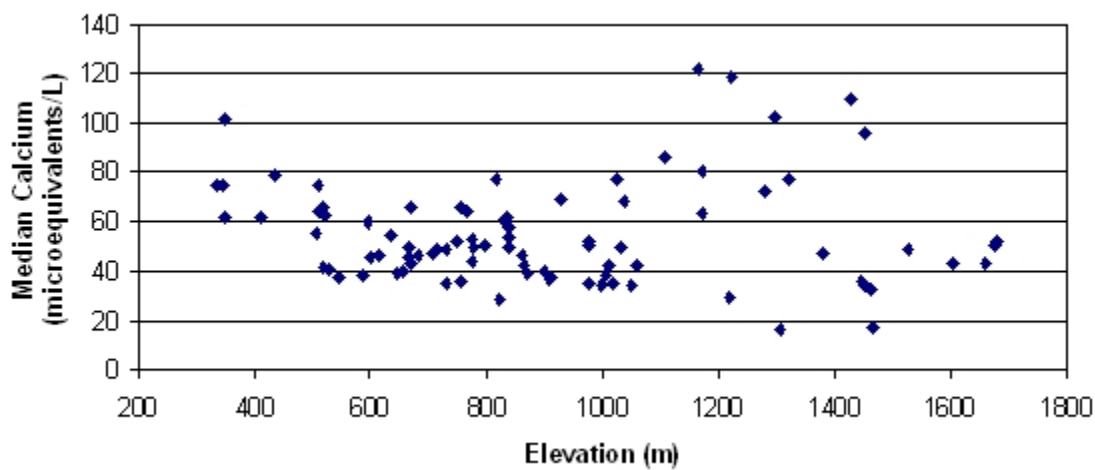


Figure 3-25. Scatter plot of median calcium in sampled GRSM streams without Cades Cove sites

Harwell, using stream survey data from October, 1993 to October, 1998, found 71 of the 90 sites (78.9%) to have median pH values greater than 6.0, which corresponds exactly to the results above. Although these sites have pH values on the acidic side of neutral, there are generally no effects on trout species within this range, as discussed earlier in chapter II. There are seventeen sites (18.9%) with pH values in the range of 5.0 to 6.0. Harwell found sixteen sites in this pH range (17.8%). This range of pH values is likely to be harmful to trout species when aluminum concentrations exceed about 0.2 mg/l. The lower end of this range is probably harmful to the eggs and fry of trout and also to non-acclimated trout especially when calcium, sodium, and chloride concentrations are low. Only two of the ninety sampling sites have median pH values in the 4.5 to 5.0 range. Harwell's work produced three sampling sites with median pH values in this range (Harwell, 2001). This pH range is likely harmful to eggs, fry and adult trout, particularly in the soft water conditions prevalent in the GRSM. Aluminum concentrations greater than around 0.2 mg/l can increase the harmful effects to trout in the pH range 4.5 to 5.0. Currently, there are no sampling sites with median pH values less than 4.5, although pH values could be lowered by as much as 1 pH unit during high-flow episodic events depending upon the acid neutralizing capacity in the stream. It can be seen through the comparisons to Harwell's work that median pH values have changed little with the addition of three years of data (1999 - 2001). Although there are 19 sampling sites with pH values less than 6.0 (see figure 3-26 for map of these sites), below which there may be adverse effects on trout populations, seven of these sampling sites are high elevation springs, which probably do not have a physical environment suitable for trout populations

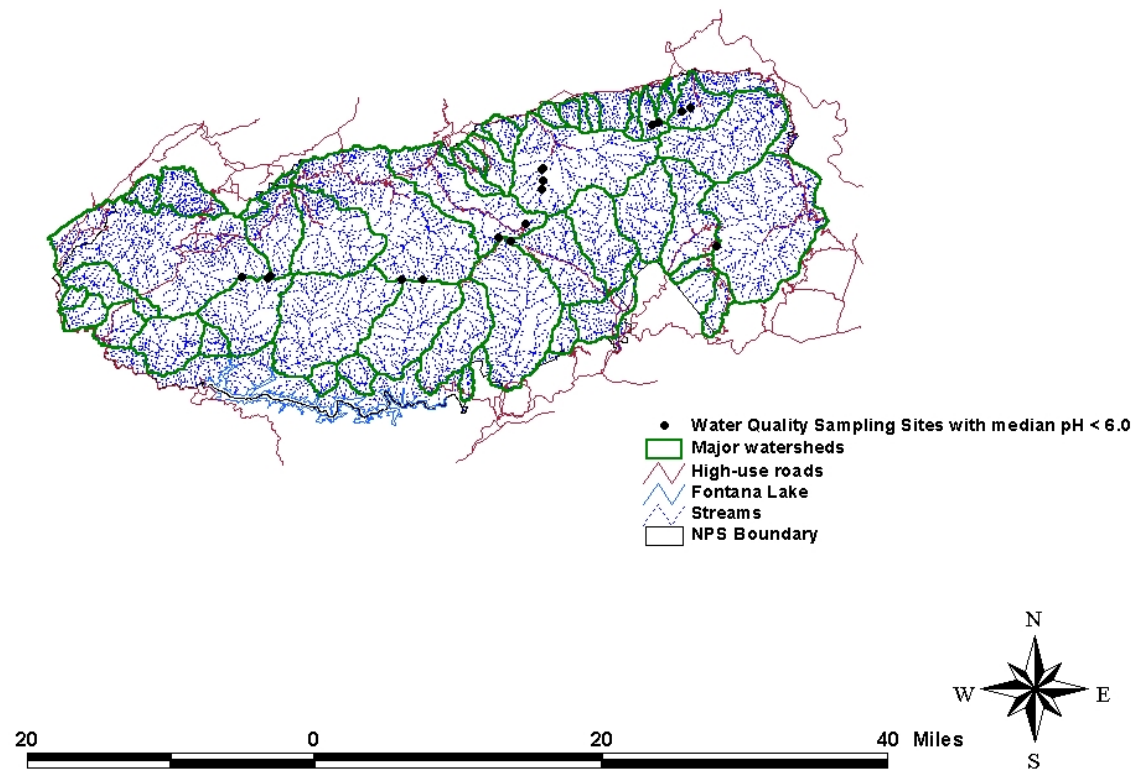


Figure 3-26. Map of sampling sites with pH < 6.0

even if pH values were ideal. Of the six sampling sites with median pH values less than 5.5, only two (237 and 252) are not high elevation springs. Sampling site 237 is a high elevation site in the west prong of the Little River watershed on Walker Camp prong. Sampling site 252 is located directly below a road cut for U.S. Highway 441 on Beech Flats Creek within the Oconaluftee watershed. Sampling site 253 is located directly above this same road cut and has a median pH value of 6.43, while 252 has a median pH value of 5.01. This is a decrease of 1.42 pH units in the distance it takes for Beech Flats Creek to flow under U.S. Highway 441 (<200 meters). This dramatic decrease in pH can most likely be attributed to exposed anakeesta geology due to the road cut.

From table 3-3, it can be seen that median pH values can vary from a minimum value of 4.82 to a maximum of 7.43. This represents over a 2.5 order of magnitude difference in hydrogen ion concentrations, which indicates that pH varies greatly within the GRSM. Figure 3-1 shows a histogram of the median pH values. The plot resembles a somewhat normal distribution with the exception of the 6.25 to 6.50 pH range, which contains a large number of the sampling sites.

Inspection of the box plot in figure 3-2 reveals that generally, pH values decrease with increases in elevation. Simple linear regression performed on the data indicates a statistically significant ($p < 0.05$) trend in median pH with elevation. The scatter plot, trend line, and regression equation are displayed in figure 3-3. Elevation explains about 51 percent of the variability in pH ($r^2 = 0.505$). The regression equation obtained from the data is as follows:

$$\text{Median pH} = -9.237 \text{ E-04 (elevation)} + 7.078.$$

where elevation is in meters above sea level. This equation shows that pH drops 0.1 units for every 108 meter increase in elevation.

Acid Neutralizing Capacity

The variability of acid neutralizing capacity (ANC) within the GRSM is similar to that of pH because pH values are positively correlated with ANC (Pearson correlation coefficient of 0.743 significant at 0.01 level). Table 3-4 lists the ANC ranges that are commonly cited to classify the acidic level of a surface water, its classification, and the percentage of sample sites within each range for the current data. It can be seen that 87 of the 90 sites (about 97%) are classified as either sensitive, extremely sensitive, or acidic.

This indicates that the majority of sampling sites have little resistance to acidified runoff encountered during episodic events, which can detrimentally affect trout populations in those streams supporting such organisms.

Figure 3-4 shows the box plot of ANC versus elevation class and figure 3-5 shows the scatter plot of median ANC versus elevation. Like pH, ANC increases with decreasing elevation. Both the intercept and the slope prove to be statistically significant when simple linear regression is performed on the data in figure 3-5, but the equation does not explain much of the variability in ANC ($r^2=0.11$). However, when the Cades Cove sites, which have high ANC values due to influence of limestone geology, are excluded (see figure 3-6), the equation explains 38 percent of the variability in median pH.

Table 3-4. Summary of acidic level of water at sampled sites

Source: Webb, J.R., B.J. Cosby, J.N. Galloway, and G.M. Hornberger, Acidification of Native Brook Trout Streams in Virginia, *Water Resources Research*, 25(6), 1,367-1,377.

ANC range (eq/L)	Classification	Percentage of sample sites with median ANC within range
< 0	acidic	4.4*
0 - 50	extremely sensitive	54.4**
50 - 200	sensitive	37.7
> 200	not classified	3.3

* Two of the four are high elevation springs

** Five of the forty-nine are high elevation springs

Conductivity

Eighty-five of the ninety sampling sites (about 95%) within the GRSM have conductivity values less than 25 micro siemens per centimeter, which indicates that the majority of waters in the park have low ionic strengths. Three sampling sites with the highest values of median conductivity are all located within the Abrams Creek watershed, which is characterized by limestone geology as indicated by high ANC values at these sites. The other two sampling sites with the next highest values of median conductivity are located below the road cut on Beech Flats Creek within the Oconaluftee watershed. These sites have elevated sulfate concentrations due to exposed anakeesta at the road cut.

Figure 3-7 shows the variability of conductivity with respect to elevation ranges and figure 3-8 is a scatter plot of median conductivity versus elevation. There was no statistically significant relationship found between median conductivity and elevation.

Nitrate

Figures 3-9 and 3-10 show a significant trend in nitrate concentrations with elevation. The median nitrate concentrations increase with increases in elevation. Regression analysis of median nitrate versus elevation reveals a statistically significant trend with an r-square equal to 0.48. However, the regression equation yields an intercept of -3.208E-02, which gives negative nitrate concentrations for elevations below 252 meters. Therefore, this equation could not be used to predict nitrate concentrations at elevations below 252 meters.

Sulfate

Median sulfate concentrations, like nitrate, increase with elevation up to about 1372 meters, but then begin to decrease and remain fairly constant with increases in elevation. This is illustrated in figure 3-11. Regression analysis (see figure 3-12 for scatter plot) proved both the slope and intercept, from the resulting equation, to be statistically significant ($p < 0.05$). However, only 3.9 % of the variability in sulfate is explained by elevation indicating that elevation alone is not a good predictor of sulfate concentrations. The slope term of the resulting regression equation is positive, which indicates that sulfate concentrations might increase with elevation. The spatial variability in sulfate concentrations are most likely due to anakeesta geology (Harwell, 2001).

Chloride

The majority of sampling sites within the GRSM (about 97 %) have median chloride concentrations less than 20 micro-equivalents per liter and show very little variability with elevation (see figure 3-13). Many studies indicate that higher

concentrations (> 1 milli-equivalent) of chloride, sodium, potassium, and calcium may help trout to better cope with stress caused by ionoregulatory dysfunction at pH values below 6.0 (see chapter II) and chloride concentrations of this low magnitude would probably aid trout populations very little. A scatter plot of median chloride concentration versus elevation can be seen in figure 3-14. Regression analysis of this data did not yield a statistically significant trend.

Sodium

Figure 3-15 shows box plots of sodium concentration versus elevation ranges. The box plots indicate a decreasing trend in sodium with increases in elevation except for elevations in the 1372 to 1676 meter range which are a little higher than surrounding elevations. It can also be seen that median sodium concentrations are generally less than 40 eq/l. It is likely that concentrations this low would not help trout populations compensate for an increased sodium efflux, which they experience during ionoregulatory dysfunction brought on by low environmental pH. As discussed earlier, one study (Packer and Dunson, 1970) found that rainbow trout exposed to pH 3.5 survived over three times longer in a solution of 150 meq/l than the rainbow trout in a solution of 100 eq/l. Figure 3-16 shows a scatter plot of median sodium concentrations versus elevation. Regression analysis reveals a statistically significant trend for sodium, but only 18 percent of the variability in concentrations are explained by elevation. The regression equation yields a negative slope, indicating that sodium concentrations might decrease with increases in elevation, but more of the variability needs to be explained.

Potassium

Inspection of the box plots in figure 3-17 reveals that potassium varies very little with elevation and that all median values are less than 20 eq/l. Potassium is a nutrient that is also suspected to be lost during periods of ionoregulatory dysfunction in trout species and ambient concentrations of this magnitude, like sodium and chloride, would probably help trout compensate little for the loss (refer to chapter II). Figure 3-18 is a scatter plot of median potassium concentrations versus elevation. Regression analysis reveals a statistically significant decreasing trend in median potassium with elevation, but only 8 percent of the variability is explained by elevation alone.

Ammonium

The median ammonium ion concentrations for every sampling site are below our detection limit. However, figure 3-19, which presents box plots of ammonium concentration versus elevation class, does show that ammonium concentrations above the detection limit are occasionally encountered.

Magnesium

Median concentrations of magnesium show no significant trends with elevation. Figures 3-20 and 3-21 present this graphically. From these figures, it can be seen that median concentrations of magnesium remain fairly constant with elevation with the exception of three sampling sites on Abrams creek within Cades Cove. These sites have relatively high concentrations of magnesium and calcium most likely because of underlying limestone geology. Figure 3-24 presents a scatter plot of the data with the exclusion of the Cades Cove sites. Statistical analysis of the median magnesium values

without the Abrams Creek sites yields an average of 27.5 eq/L with a standard deviation of 12.2 eq/L for magnesium, which indicates that magnesium concentrations throughout the park are quite low.

Calcium

Median concentrations of calcium also show no significant trends with elevation. Figures 3-22 and 3-23 present this graphically. From these figures, it can also be seen that median concentrations of calcium remain fairly constant with elevation with the exception of three sampling sites on Abrams Creek. Figure 3-25 presents a scatter plot of the data with the exclusion of the Cades Cove sites. Statistical analysis of the median calcium values without the Abrams Creek sites yields an average of 54.8 eq/L with a standard deviation of 20.7 eq/L. As mentioned previously in chapter II, calcium plays an important role in vital trout physiological processes. Although no specific calcium criteria values could be found in literature, this author suspects that the majority of the park has calcium concentrations too low to help trout deal with low pH stress, particularly when other ionic concentrations are low, which is characteristic of the soft waters found within the GRSM.

Conclusions

The following observations and conclusions were made from the results presented earlier in this chapter:

1. About 79% of the ninety sampling sites were found to have median pH values above 6.0, which also corresponds to the pH above which generally has no effects on trout species. This percentage of sampling sites

corresponds exactly with the results found by Harwell (2001).

2. About 19% of the sampling sites were found to have median pH values in the 5.0 to 6.0 range. This pH range is likely to be harmful to trout species (refer to chapter II). Harwell (2001) found about 18% of the sites to be in this range.
3. Only two of the ninety sampling sites produced median pH values in the 4.5 to 5.0 range. Harwell's work produced 3 sampling sites in this range. This pH range is also likely to be harmful to trout species (refer to chapter II), but both of these sites are high elevation springs which do not have suitable physical environments for trout species.
4. There are no sampling sites with median pH values under 4.5, although pH values could be lowered by more than 1 pH unit during high-flow episodic events. Depending upon the duration of the event, pH values below 4.5 could be detrimental to trout populations.
5. About 97% of the ninety sampling sites have median ANC values under 200 microequivalents per liter, which indicates that the majority of streams in the GRSM have little resistance to acidified runoff encountered during episodic events.
6. Regressions performed on pH, ANC, sodium, and potassium yielded statistically significant decreasing trends with elevation. Therefore, not only do the pH conditions worsen for trout species as elevation increases, but much needed nutrients also decrease, which can help to exacerbate the

negative effects of low pH.

7. Regressions on nitrate and sulfate yield statistically significant increasing trends with elevation. This was expected given the decreasing trends in pH and ANC.
8. Neither magnesium or calcium yielded any significant trends with elevation. However, the average median of their values are quite low at 27.5 and 54.8 microequivalents per liter for magnesium and calcium respectively.
9. There were no statistically significant trends with elevation for conductivity and chloride.

Chapter IV. Water Quality Modeling

The following chapter deals with the modeling of important water quality constituents affected by acid deposition. The purpose of which to find what physical and temporal characteristics drive water quality conditions in the GRSM. Harwell (2001) evaluated the modeling of various analytes and developed statistically significant regressions. The work herein attempts to improve on Harwell's work by incorporating three additional years of data and hydrologic, precipitation, and deposition data.

Data

The data set used in this chapter is same as described in chapter 3. The following water quality constituents were chosen for modeling due to their importance in acid deposition and stream health: pH, acid neutralizing capacity (ANC), nitrate, and sulfate.

Table 4-1 lists the independent variables used in the modeling process and a brief description of each variable. The average basin slope, stream order, percent Limestone, and percent Anakeesta were obtained for each sampling site from previous work conducted by Harwell (2001). Other variables compiled by Harwell such as basin length, stream density, and vegetation cover were not included because they only occurred infrequently if at all in Harwell's regressions. Flows from the Little River and Cataloochee Creek were obtained for the days of sample collection from USGS gauging stations. Daily precipitation values were obtained for each sampling location from the closest National Weather Service weather station for the day of sampling to five days prior to sampling to account for antecedent conditions. The NWS weather stations are located at the GRSM Park Headquarters, Cades Cove, Newfound Gap, Mount LeConte,

Table 4-1. Description of regression variables

Variable	Description
Cumulative Julian Date	Julian date counted from 1/1/1900
Sine Theta	Theta = 2 * (fraction of a year), sine and cosine functions used to model seasonal fluctuations in water quality parameter
Cosine Theta	
Elevation (meters)	Elevation of sampling site in meters above mean sea level obtained from USGS quads
Precipitation Code	0 - no precipitation in the 48 hours preceeding sample collection, 1 - some precipitation
Little River Flow (cfs)	Average daily flow measurements from USGS gauging stations on the day of sampling
Cataloochie Flow (cfs)	
Number of Days Since Last Prec.	The number of days preceeding sample collection since a measureable precipitation occurred at the closest of the five National Weather Service weather stations within the park.
Stream Order	Stream order for sampling site using Hortons method (USGS quads)
Avg. Basin Slope (%)	Average land slope of the contributing area (GIS)
Percent Limestone	Percentage of contributing area (geology type); Geology information unavailable for sites within Hazel Creek watershed
Percent Anakeesta	
Closest Precipitation (0)	The precipitation at the closest NWS weather station to the sampling site in inches for the same day as sample collection (0), 1 day prior (1), 2 days prior (2), 3 days prior (3), 4 days prior (4), and 5 days prior (5).
Closest Precipitation (1)	
Closest Precipitation (2)	
Closest Precipitation (3)	
Closest Precipitation (4)	
Closest Precipitation (5)	
Total Monthly TF Noland Prec. (in)	Data obtained from an intensive monitoring site at the Noland Divide watershed within the GRSM. TF - through fall (precipitation collected under forest canopy), OS - open site (precipitation collected out in the open)
Total TF Monthly Flux NO3	
Total TF Monthly Flux SO4	
Total TF Monthly Flux H	
Total Monthly OS Noland Prec. (in)	
Total OS Monthly Flux NO3	
Total OS Monthly Flux SO4	
Total OS Monthly Flux H	

and Oconaluftee. The total monthly precipitation and fluxes of hydrogen ion, sulfate, and nitrate were obtained for the sample collection months from an acid deposition monitoring site at the Noland Divide watershed within the GRSM

Methods of Analysis

Stepwise multiple linear regression was used to model pH, ANC, nitrate and sulfate using the independent variables in table 4-1. Models for these constituents were developed using data for all of the sampling sites with elevation included as an independent variable. Also, models were developed for the water quality constituents using data for sampling sites within elevational groups since much of the variability in constituent values can be explained by elevation alone (see chapter III) and elevation was not included as an independent variable. The elevation classes are presented in table 4-2 with the number of sampling sites within each elevation range.

The water quality constituents (pH, ANC, nitrate, and sulfate) were modeled using the stepwise multiple linear regression platform in SPSS. All independent variables were used in the first step of the modeling process. The variables were set to enter the model if the probability of the partial F statistic was less than or equal to 0.05 and set to leave if the partial F statistic was greater than or equal to 0.10. These entry and exit criteria were used for all models. Only models with significance levels less than or equal to a p-value of 0.05 were considered, insuring that the overall models are statistically significant. A criteria was also set that each of the independent variables in the model be statistically significant at a p-value of 0.10, but in actuality all independent variables included in the models found were significant to a p-value of 0.05.

Table 4-2. Elevation classes

Elevation class	Range of elevation, in meters above mean sea level	Range of elevation, in feet above mean sea level	Number of sampling sites
1	less than 305	less than 1000	0
2	305-457	1000-1500	7
3	457-610	1500-2000	13
4	610-762	2000-2500	16
5	762-914	2500-3000	18
6	914-1,067	3000-3500	13
7	1,067-1,219	3500-4000	4
8	1,219-1,372	4000-4500	6
9	1,372-1,524	4500-5000	7
10	1,524-1,676	5000-5500	3
11	greater than 1,676	greater than 5500	3

Multicollinearity concerns were addressed using the variance inflation factor (VIF) and informal multicollinearity diagnostics such as Spearman and Pearson bivariate correlations and theoretical and experience driven considerations. The VIF is ideally equal to one when the independent variable being diagnosed is not linearly related to any of the other independent variables. The largest VIF value among the independent variables is often used as an indicator of the severity of multicollinearity. A VIF value in excess of 10 is frequently taken as an indication that multicollinearity may be unduly influencing the least squares estimates (Neter et al., 1996). Independent variables with high multicollinearity were systematically removed from the models to produce the best adjusted R-square values with minimal effects of multicollinearity. Models with higher adjusted R-square values explain more of the variability in the dependent variable and are therefore preferable given that the other regression diagnostics are acceptable.

Harwell (2001) performed several procedures to evaluate the regression results. As explained by Harwell, the influences of individual observations on the models selected by stepwise regression were then evaluated by comparing each observation's Cook's D statistic and through observation of partial regression plots. Partial regression plots are useful for detecting influential data and can reveal nonlinearity (Fox, 1997). Influence is defined as observations which have both high leverage and large outliers (Helsel and Hirsch, 1992). These observations exert a strong influence on the regression model. A set value of the Cook's D statistic to measure influence was not used. Cook's D values for individual observations were observed and ones that appeared unreasonably large in comparison to other observations were noted. If inspection of partial regression

plots showed an observation which had an unreasonably high Cook's D statistic also appeared as an outlier, then it was concluded that the observation was exerting a strong influence on the model. If removal of that observation could be well-justified, then it was considered for removal from the analysis. If its removal improved the amount of variability explained by the model and the model adhered to the assumptions of regression, then it was removed.

Then other important regression assumptions were addressed. Randomness of the residuals was checked using partial residual plots. The residuals were plotted by each of the independent variables. The points should be randomly distributed about the horizontal axis with a proportionate amount above and below zero. Normality of the residuals was checked using the Shapiro-Wilk test and observation of the normal probability plot. Partial regression or leverage plots were also observed to insure a linear relationship exists between the independent variable and the dependent variable when the other independent variables have been accounted for.

The reasonableness of predicted constituent values was also checked. Reasonable predicted values were defined as not negative. The model should not predict negative values for water quality constituents. The only exception to this would be the model to predict ANC. Values for ANC can be negative. Since pH values greater than 8 are rarely encountered in the GRSM, the predicted maximum values for pH should also not exceed 8.

The principle of parsimony was also used in the model selection process. This principle is used for choosing among models or theories and denotes that, everything else

being equal, simpler models are better (DeLurgio, 1998). Therefore, the simplest model that explains a comparable amount of the variability and adheres to the assumptions of regression was chosen as the best model.

Results

Table 4-3 presents the best model obtained for each water quality constituent as well as the adjusted R-square value and overall model p-value for all sampling sites within the Park. Tables 4-4 through 4-12 present the results for elevation classes 2 through 10. No significant models were obtained for elevation class 11. Table 4-13 presents the ranges encountered for each independent variable. Figures 4-1 through 4-5 present scatter plots of the predicted water quality constituent values versus the actual values for pH, ANC, ANC without Cades Cove sites, nitrate, and sulfate, respectively, for all sampling sites.

Discussion of Results

The modeling results for each water quality parameter will be discussed in the following order: pH, ANC, nitrate, and sulfate. The overall model p-values were significant to a level of 0.05 and regression assumptions were satisfactory for all of the models discussed in the following.

pH

The pH model for all elevation classes produced an adjusted R-square value of 0.706, which means that 70.6 percent of the variability in pH is explained by the model. The model shows that stream water pH (see table 4-3) increases with increases in the percentage of the contributing area containing underlying limestone geology, which is

Table 4-3. Model results for all elevation classes

Constituent	Model	Adjusted r²	Model p
pH	$9.10 + (4.08\text{E-}02 * \% \text{ limestone}) + (-1.47\text{E-}02 * \text{avg. basin slope in } \%) + (-3.64\text{E-}04 * \text{Little River flow in cfs}) + (-7.23\text{E-}04 * \text{elevation in meters}) + (-4.38\text{E-}05 * \text{cumulative julian date}) + (-8.90\text{E-}02 * \cosine \theta) + (-6.03\text{E-}02 * \text{closest precipitation (5) in inches})$	0.706	0.000
ANC (eq/L)	$110.70 + (5.48\text{E+}01 * \% \text{ limestone}) + (-7.57\text{E-}02 * \text{Little River flow in cfs}) + (-2.82\text{E+}01 * \sin \theta) + (-5.63\text{E+}01 * \text{closest precipitation (0) in inches}) + (1.73\text{E+}01 * \text{stream order}) + (-2.09\text{E+}00 * \text{avg. basin slope in } \%)$	0.856	0.000
Nitrate (eq/L)	$-18.23 + (1.50\text{E-}02 * \text{Little River flow in cfs}) + (5.49\text{E-}01 * \text{avg. basin slope in } \%) + (3.62\text{E-}02 * \text{total Noland monthly OS flux of H})$	0.272	0.000
Sulfate (eq/L)	$29.17 + (-5.30\text{E-}02 * \text{elevation in meters}) + (6.32\text{E-}01 * \text{avg. basin slope in } \%) + (2.28\text{E-}02 * \text{Little River flow in cfs}) + (-4.98\text{E+}00 * \sin \theta) + (4.11\text{E+}00 * \text{closest precipitation (5) in inches}) + (4.79\text{E+}00 * \text{closest precipitation (3) in inches})$	0.238	0.000

Table 4-4. Model results for elevation class 2: 305-457 meters (1000-1500 feet)

Constituent	Model	Adjusted r ²	Model p
pH	$9.03 + (-2.65\text{E-}02 \cdot \text{avg. basin slope in \%}) + (-2.33\text{E-}04 \cdot \text{Little River flow in cfs}) + (-9.34\text{E-}02 \cdot \cos \theta) + (3.30\text{E-}02 \cdot \text{\% limestone}) + (-7.45\text{E-}02 \cdot \text{closest precipitation (5) in inches}) + (-3.49\text{E-}05 \cdot \text{cumulative julian date}) + (-1.15\text{E-}01 \cdot \text{closest precipitation (0) in inches}) + (-4.38\text{E-}02 \cdot \sin \theta)$	0.670	0.000
ANC (eq/L)	$578.25 + (4.57\text{E+}01 \cdot \text{\% limestone}) + (-6.27\text{E-}02 \cdot \text{Little River flow in cfs}) + (-1.62\text{E-}02 \cdot \text{cumulative julian date}) + (3.29\text{E+}00 \cdot \text{\# of days since last precipitation}) + (-2.71\text{E+}01 \cdot \sin \theta) + (-2.27\text{E+}01 \cdot \cos \theta) + (1.80\text{E+}01 \cdot \text{stream order})$	0.734	0.000
Nitrate (eq/L)	$-5.01 + (1.59\text{E+}00 \cdot \text{avg. basin slope in \%}) + (1.68\text{E-}02 \cdot \text{Little River flow in cfs}) + (-2.74\text{E+}00 \cdot \text{stream order}) + (-2.10\text{E+}00 \cdot \cos \theta)$	0.687	0.000
Sulfate (eq/L)	$100.17 + (1.58\text{E+}00 \cdot \text{avg. basin slope in \%}) + (-1.06\text{E+}01 \cdot \text{stream order}) + (-2.63\text{E+}00 \cdot \sin \theta) + (3.78\text{E+}00 \cdot \text{closest precipitation (5) in inches}) + (1.33\text{E+}01 \cdot \text{closest precipitation (3) in inches}) + (1.00\text{E+}01 \cdot \text{closest precipitation (0) in inches}) + (7.34\text{E+}00 \cdot \text{closest precipitation (1) in inches}) + (-2.29\text{E-}03 \cdot \text{cumulative julian date})$	0.551	0.000

Table 4-5. Model results for elevation class 3: 457-610 meters (1500-2000 feet)

Constituent	Model	Adjusted r²	Model p
pH	$8.87 + (4.26\text{E-}02 * \% \text{ limestone}) + (-3.47\text{E-}04 * \text{Little River flow in cfs}) + (-1.32\text{E-}02 * \text{avg. basin slope in \%}) + (-8.23\text{E-}02 * \text{cosine theta}) + (-5.09\text{E-}05 * \text{cumulative julian date})$	0.715	0.000
ANC (eq/L)	$89.55 + (5.77\text{E+}01 * \% \text{ limestone}) + (-3.01\text{E+}01 * \text{sine theta}) + (-1.20\text{E-}01 * \text{Little River flow in cfs})$	0.881	0.000
Nitrate (eq/L)	$-15.39 + (3.70\text{E+}00 * \text{closest precipitation (2) in inches}) + (-3.22\text{E-}01 * \% \text{ anakeesta}) + (7.39\text{E-}01 * \text{avg. basin slope in \%}) + (2.85\text{E+}00 * \text{sine theta})$	0.362	0.000
Sulfate (eq/L)	$136.454 + (5.97\text{E+}00 * \text{stream order}) + (-3.58\text{E-}03 * \text{cumulative julian date}) + (4.69\text{E+}00 * \text{closest precipitation (2) in inches})$	0.115	0.000

Table 4-6. Model results for elevation class 4: 610-762 meters (2000-2500 feet)

Constituent	Model	Adjusted r²	Model p
pH	10.38 + (-3.66E-02*avg. basin slope in %) + (9.60E-02*stream order) + (-2.45E-04*Little River flow in cfs) + (-7.13E-05*cumulative julian date) + (-1.04E-01*closest precipitation (1) in inches) + (-5.92E-02*closest precipitation (2) in inches)	0.775	0.000
ANC (eq/L)	151.14 + (-2.88E+00*avg. basin slope in %) + (1.61E+01*stream order) + (-9.55E+00*sine theta) + (-3.80E-01*% anakeesta) + (-2.45E-02*Little River flow in cfs)	0.609	0.000
Nitrate (eq/L)	-29.79 + (9.29E-01*avg. basin slope in %) + (1.88E-02*Little River flow in cfs) + (-2.51E+00*stream order) + (5.15E-02*total Noland monthly OS flux of SO ₄)	0.484	0.000
Sulfate (eq/L)	51.47 + (1.91E+00*avg. basin slope in %) + (7.12E+00*closest precipitation (1) in inches) + (-3.15E-03*cumulative julian date)	0.649	0.000

Table 4-7. Model results for elevation class 5: 762-914 meters (2500-3000 feet)

Constituent	Model	Adjusted r²	Model p
pH	9.12 + (-5.32E-05*cumulative julian date) + (-2.23E-02*avg. basin slope in %) + (8.82E-02*stream order) + (-2.90E-04*Little River flow in cfs) + (-2.35E-03*% anakeesta) + (-5.32E-05*cumulative julian date) + (-6.40E-02*closest precipitation (2) in inches)	0.610	0.000
ANC (eq/L)	317.49 + (-1.79E+00*avg. basin slope in %) + (-7.24E+00*sine theta) + (1.04E+01*stream order) + (-2.38E-01*% anakeesta) + (-2.81E-02*Little River flow in cfs)+ (-5.70E-03*cumulative julian date)	0.616	0.000
Nitrate (eq/L)	-53.64 + (1.48E+00*avg. basin slope in %) + (5.63E-01*total monthly Noland OS precipitation in inches) + (-1.44E-01*% anakeesta) + (3.60E+00*closest precipitation (1) in inches)	0.489	0.000
Sulfate (eq/L)	37.69 + (1.59E+00*avg. basin slope in %) + (3.21E-01*% anakeesta) + (5.26E+00*closest precipitation (1) in inches) + (1.59E+00*stream order) + (-2.46E-03*cumulative julian date)	0.834	0.000

Table 4-8. Model results for elevation class 6: 914-1067 meters (3000-3500 feet)

Constituent	Model	Adjusted r²	Model p
pH	8.76 + (-1.75E-02*avg. basin slope in %) + (-1.28E-01*closest precipitation (2) in inches) + (-1.42E-01*closest precipitation (1) in inches) + (-6.72E-02*sine theta) + (-4.79E-05*cumulative julian date)	0.414	0.000
ANC (eq/L)	82.12 + (-1.02E+00*avg. basin slope in %) + (-9.84E+00*sine theta) + (-6.81E+00*closest precipitation (1) in inches)	0.314	0.000
Nitrate (eq/L)	45.18 + (6.81E-01*avg. basin slope in %) + (3.75E+00*sine theta) + (-5.81E-02*% anakeesta) + (3.80E+00*closest precipitation (1) in inches) + (3.20E-01*number of days since last precipitation) + (-1.55E-03*cumulative julian date)	0.257	0.000
Sulfate (eq/L)	-22.34 + (2.03E+00*avg. basin slope in %) + (1.74E+01*stream order) + (1.48E-01*% anakeesta) + (7.04E+00*closest precipitation (5) in inches) + (3.07E+00*cosine theta) + (-2.28E-03*cumulative julian date)	0.781	0.000

Table 4-9. Model results for elevation class 7: 1067-1219 meters (3500-4000 feet)

Constituent	Model	Adjusted r ²	Model p
pH	$10.50 + (-9.79\text{E-}04 \cdot \text{Little River flow in cfs}) + (-7.59\text{E-}02 \cdot \text{avg. basin slope in \%})$	0.697	0.000
ANC (eq/L)	$558.96 + (-7.24\text{E-}02 \cdot \text{Little River flow in cfs}) + (-9.28\text{E+}00 \cdot \text{avg. basin slope in \%}) + (-1.27\text{E+}01 \cdot \text{sine theta})$	0.610	0.000
Nitrate (eq/L)	$33.81 + (1.56\text{E-}02 \cdot \text{Little River flow in cfs}) + (7.66\text{E+}00 \cdot \text{closest precipitation (4) in inches}) + (-5.14\text{E-}02 \cdot \% \text{ anakeesta})$	0.333	0.000
Sulfate (eq/L)	$-54.98 + (3.40\text{E-}01 \cdot \% \text{ anakeesta})$	0.593	0.000

Table 4-10. Model results for elevation class 8: 1219-1372 meters (4000-4500 feet)

Constituent	Model	Adjusted r ²	Model p
pH	5.48 + (-1.20E-03*Little River flow in cfs) + (3.64E-01*stream order) + (1.44E-01*precipitation code)	0.616	0.000
ANC (eq/L)	-3.88 + (18.3*stream order) + (-0.0884*Cataloochie flow in cfs)	0.445	0.000
Nitrate (eq/L)	59.32 + (-1.40E+01*stream order) + (4.86E-02*Cataloochie flow in cfs)	0.441	0.000
Sulfate (eq/L)	659.12 + (-1.14E+01*avg. basin slope in %) + (3.47E-01*% anakeesta)	0.447	0.000

Table 4-11. Model results for elevation class 9: 1372-1524 meters (4500-5000 feet)

Constituent	Model	Adjusted r²	Model p
pH	$8.39 + (-5.62\text{E-}02 * \text{avg. basin slope in \%}) + (-2.48\text{E-}04 * \text{cumulative julian date})$	0.506	0.000
ANC (eq/L)	$665.09 + (-2.05\text{E+}00 * \text{avg. basin slope in \%}) + (-1.56\text{E-}02 * \text{cumulative julian date})$	0.308	0.000
Nitrate (eq/L)	$35.64 + (-2.44\text{E+}01 * \text{stream order}) + (9.93\text{E-}01 * \text{avg. basin slope in \%}) + (4.24\text{E+}00 * \text{cosine theta})$	0.562	0.000
Sulfate (eq/L)	$-30.25 + (5.78\text{E+}00 * \text{avg. basin slope in \%}) + (-8.67\text{E+}01 * \text{stream order})$	0.279	0.000

Table 4-12. Model results for elevation class 10: 1524-1676 meters (5000-5500 feet)

Constituent	Model	Adjusted r ²	Model p
pH	$6.32 + (-1.26\text{E-}02 * \text{total Noland monthly OS flux of NO}_3)$	0.299*	0.006
ANC (eq/L)	$40.76 + (-6.66\text{E-}01 * \text{total Noland monthly OS flux of NO}_3)$	0.237*	0.023
Nitrate (eq/L)	$-65.79 + (3.09\text{E+}00 * \text{avg. basin slope in \%})$	0.177*	0.046
Sulfate (eq/L)	$10.81 + (1.20\text{E-}01 * \text{total Noland monthly TF flux of H})$	0.185*	0.042

* Fewer than 30 observations

Table 4-13. Ranges for regression variables

Variable	Units	Minimum Value	Maximum Value
Cumulative Julian Date	days	34678	37213
Sine Theta		-1	1
Cosine Theta		-1	1
Elevation	meters	335	1689
Precipitation Code		0	1
Little River Flow	cfs	25	1160
Cataloochie Flow	cfs	18	556
Number of Days Since Last Prec.	days	0	32
Stream Order		1	5
Avg. Basin Slope	%	25	72
Percent Limestone	%	0	21
Percent Anakeesta	%	0	100
Closest Precipitation (0)	inches	0	2
Closest Precipitation (1)	inches	0	3
Closest Precipitation (2)	inches	0	2
Closest Precipitation (3)	inches	0	2
Closest Precipitation (4)	inches	0	2
Closest Precipitation (5)	inches	0	2
Total Monthly TF Noland Prec.	inches	1	20
Total TF Monthly Flux NO3	equivalents/month/hectare	7	181
Total TF Monthly Flux SO4	equivalents/month/hectare	61	320
Total TF Monthly Flux H	equivalents/month/hectare	27	254
Total Monthly OS Noland Prec.	inches	2	21
Total OS Monthly Flux NO3	equivalents/month/hectare	0	56
Total OS Monthly Flux SO4	equivalents/month/hectare	11	259
Total OS Monthly Flux H	equivalents/month/hectare	8	112

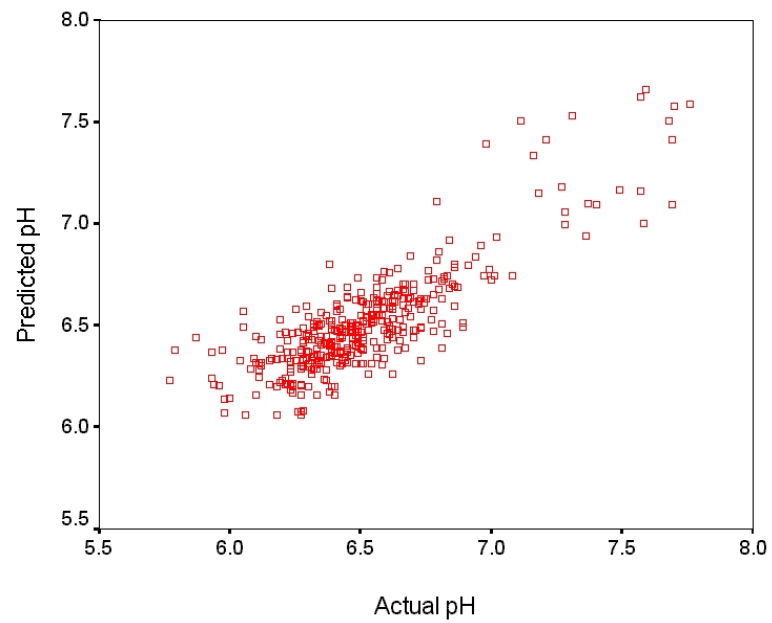


Figure 4-1. Plot of actual versus predicted pH values for all elevation classes

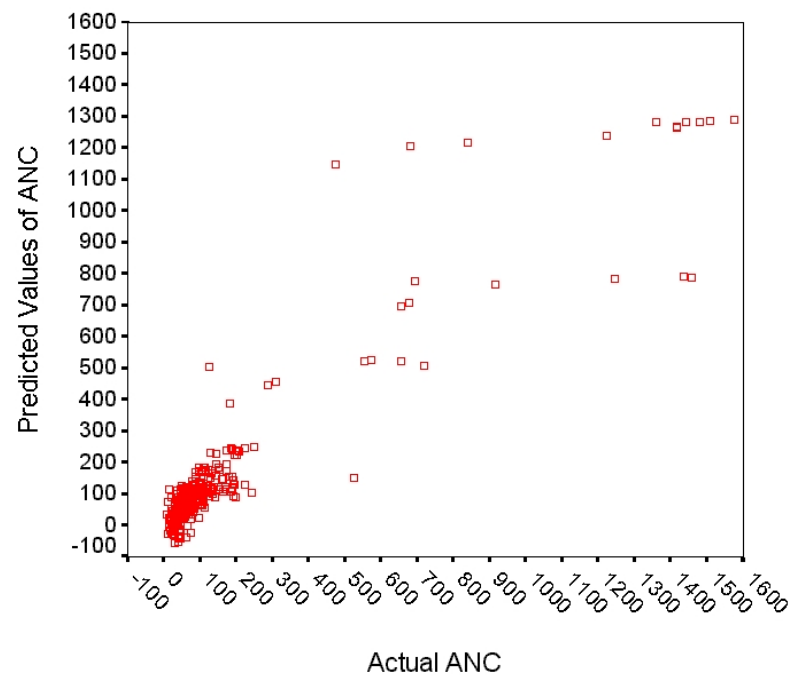


Figure 4-2. Plot of actual versus predicted ANC values for all elevation classes

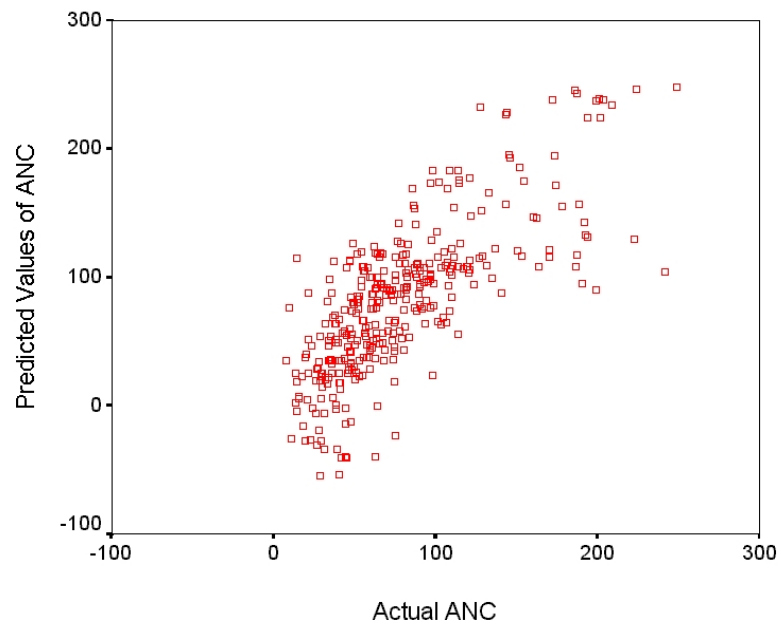


Figure 4-3. Plot of actual versus predicted ANC values for all elevation classes omitting high ANC values from Cades Cove

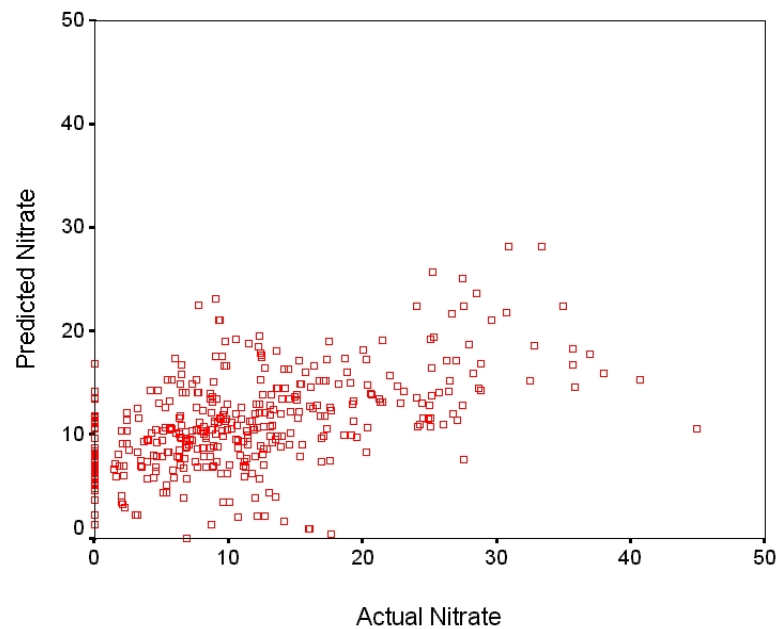


Figure 4-4. Plot of actual versus predicted nitrate values for all elevation classes

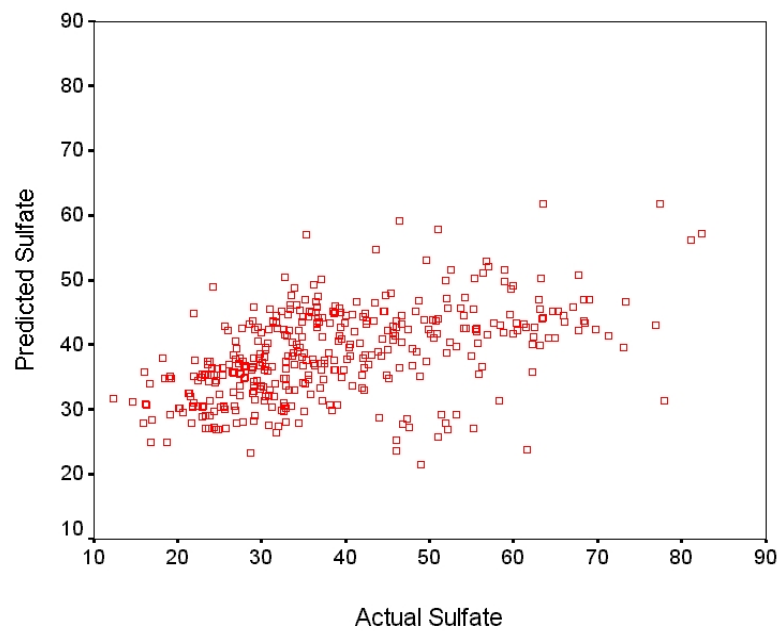


Figure 4-5. Plot of actual versus predicted sulfate values for all elevation classes

what one would expect since limestone dissolves to add carbonate species to ground water supplying surface waters. The carbonate adds to the acid neutralizing capacity of the water, which helps to raise or maintain pH values. The model shows pH to decrease with increases in the average basin slope of contributing area. Higher average basin slopes are indicative of higher elevation sites which generally have little ANC. Also, the relation between pH and average basin slope might result from the short residence times of water and the limited soil development of higher elevations (Clow and Sueker, 2000). The model also shows that pH decreases with increasing flow at the Little River gauging station which is indicative of precipitation events adding, releasing, and carrying acid causing species to the surface waters. Figure 4-6 presents some recent storm event monitoring on the West Prong of the Little River (located at the second bridge below Morton Tunnel on U.S. 441, at an elevation around 4250 feet) and shows an obvious decrease in pH with corresponding increase in stage. As discussed in chapter III, pH is found to decrease with increases in elevation. Seasonal fluctuations in pH were also indicated by the model. Values of pH were also found to decrease with time, which will be discussed in detail in the next chapter. The pH was also found to decrease with increases in prior precipitation, which is also expected in areas of acid deposition. Figure 4-1 is a scatter plot of the predicted versus actual pH values. The plot indicates a fairly good fit with scatter around a 45 degree line.

The pH modeling results for each elevation class are presented in tables 4-4 through 4-12. Elevation was not included as an independent variable in order to remove its already ascertained influence on pH. The models produced similar results to those

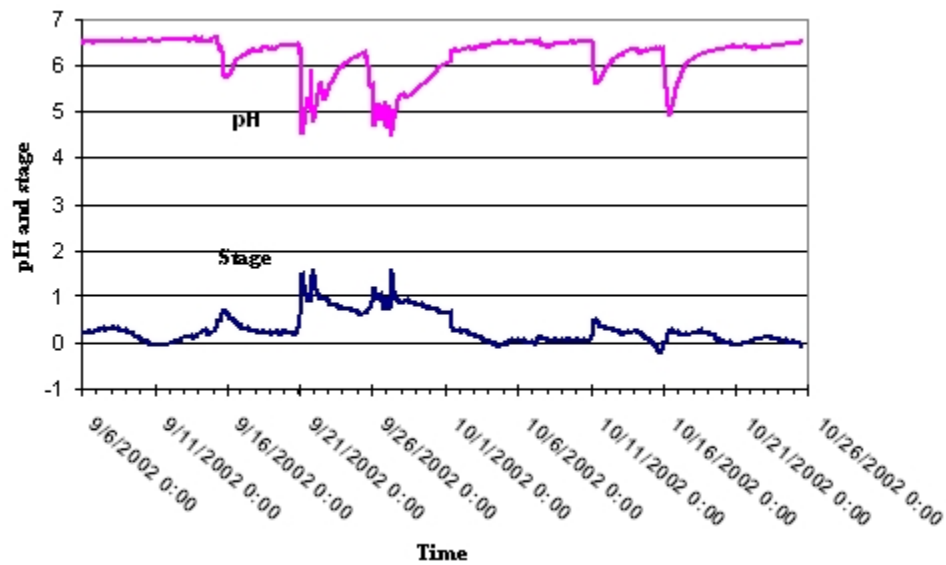


Figure 4-6. Storm events in West Prong Little Pigeon River

with all sampling sites. The adjusted R-square values ranged from 0.299 to 0.775, with higher values generally at the lower elevations, which indicates higher variability in pH at the higher elevations. Seven of the nine models included basin slope and the coefficients were all of the same order of magnitude. As before, some of the models indicated an inverse relationship in pH with Little River flow, time, and precipitation and some of the models indicated a direct relation in pH with percent limestone. In addition to these relationships, a direct relationship with pH and stream order was also found for some of the elevation classes. Higher order streams are generally found at lower elevations where ANC is higher and therefore, pH values will be higher. Also, an inverse relation in pH with the percentage of Anakeesta in the contributing area was found for some of the elevation classes. Anakeesta contains pyrite (FeS) which produces acid when placed in

contact with water, which tends to lower pH values. Elevation class 10 also indicates a decrease in pH with increases in the open site flux of nitrate at the Noland Divide, which is also a high elevation watershed. This model would be consistent with greater acid deposition since nitrate is a component. It would not be consistent with stimulating plant growth since plant uptake of nitrate consumes a proton (Freedman, 1989)

ANC

ANC modeling produced very similar results to those of pH, which was expected since the Pearson bivariate correlation between pH and ANC was found to be 0.743 and significant to an alpha level of 0.01.

The ANC model for all elevation classes (see table 4-3) produced an adjusted R-square value of 0.856. A direct relationship with ANC was found for percent limestone and stream order and an inverse relationship with Little River flow, precipitation, and average basin slope. Figures 4-2 and 4-3 show predicted versus actual ANC values with and without Cades Cove sites, respectively.

The results of the ANC modeling for specific elevation classes are presented in tables 4-4 to 4-12. The adjusted R-square values are generally better than those for the pH models at lower elevations and poorer than the pH models at higher elevations. ANC models for each elevation class were similar to those of pH. Decreasing time trends were found for ANC in elevation classes 2, 5, and 9. Also a positive relation between ANC and the number of days since the last precipitation was found, indicating that ANC is higher during longer periods of dry weather when base level ground water dominates

surface flow. Like pH, direct relationships with ANC and stream order and inverse relationships with percent Anakeesta were found. Elevation class 10 produced a negative relationship with ANC and the total monthly open site flux of nitrate at the Noland Divide.

Nitrate

The modeling of nitrate produced poorer results than those of pH and ANC. The adjusted R-square for the model of all elevation classes was only 0.272, but the model and all coefficients were significant. A positive relationship with nitrate was found for Little River flow and average basin slope, which is the opposite of their relationships with pH discussed earlier. This relationship with nitrate and pH was expected on a chemistry basis as well as statistically (Pearson bivariate correlation coefficient of -0.326 significant at a 0.01 level of nitrate with pH). Also, a direct relationship between nitrate and the total monthly flux of open site hydrogen ion at the Noland Divide was found. Figure 4-4 is a scatter plot of the predicted versus actual nitrate values. The plot indicates that the model under predicts higher values of nitrate and is also evidenced by the poor R-square. However, better models were found for some of the lower elevation classes.

In addition to the relationships mentioned above, modeling of the individual elevation classes produced direct relationships with nitrate and precipitation and open site flux of sulfate. Inverse relationships with stream order and percent Anakeesta were also encountered. The only time trend for nitrate was a decreasing one for elevation class 6.

Sulfate

The modeling of sulfate for all elevation classes produced an adjusted R-square of 0.238. Sulfate was found to decrease with increases in elevation and increase with increases in average basin slope, Little River flow, and precipitation. The scatter plot of the predicted versus actual sulfate values (figure 4-5), like nitrate, shows that the model under predicts for higher values of sulfate, but some of the individual elevation classes produced fairly good results as evidenced by higher R-square values.

In addition to the relationships mentioned above, modeling of the individual elevation classes produced direct relationships with sulfate and percent Anakeesta and throughfall flux of hydrogen ion at the Noland Divide. As mentioned before, Anakeesta produces sulfate compounds when in contact with water, so one would expect higher surface water sulfate concentrations in areas with higher Anakeesta content. Both direct and inverse relationships with stream order were found depending on the elevation class, which probably has to do with the amounts of exposed Anakeesta within those elevation classes. Decreasing time trends for sulfate were found for elevation classes 2 through 6, which is interesting since decreasing trends in pH were also found for these elevation classes. This would indicate other acid species are increasing in these elevation classes, but only a decreasing trend for nitrate in elevation class six was found.

Conclusions

The following observations and conclusions were made from the results presented earlier in this chapter:

1. The modeling of pH and ANC reveal decreases in both during higher

flows on the Little River and greater precipitation amounts. This is a good indication of the dependence of stream water pH on hydrological conditions and gives evidence to the problem of acid deposition/rain in the GRSM.

2. Regression modeling also revealed decreasing time trends in pH, which will be discussed in the next chapter.
3. Basin characteristics such as the average basin slope and the percentage of limestone in the underlying geology were found to be significant in both the pH and ANC models. Higher average basin slopes produce lower pH and ANC values. Higher average basin slopes are indicative of higher elevation sites which generally have thinner soils with little ANC and in conjunction with short residence times serves to produce acidic surface water pH values. Higher percent limestone produces both higher pH and ANC values, indicating the importance of carbonate geology on a surface water's ability to maintain a suitable environment for trout species.
4. The modeling of pH and ANC produced similar models to those of Harwell (2001) but with a few more independent variables like flow and precipitation included in the models. R-square values were almost identical.
5. Sulfate and nitrate were both found to increase with increasing average basin slope and with Little River flow. Sulfate was also found to increase with precipitation, once again indicating the importance of hydrology on

acid species in GRSM surface waters.

6. Hydrologic variables prove to be very important in the modeling of stream water quality, especially the acid species. This further proves the need for more in depth studies of storm events in the GRSM.

Chapter V. pH Time Trend Modeling

The following chapter deals with the time trend modeling of stream water pH in the GRSM. pH is one of the most important water quality indicators of stream health in areas of acid deposition and the purpose of this chapter is to determine if statistical evidence points to long term improvement or degradation of stream water quality as measured by pH. Harwell (2001) evaluated time trends for various analytes and developed statistically significant regressions for normalized pH for several of the elevation classes but with relatively low R-square values. The work herein attempts to improve on Harwell's work by incorporating three additional years of pH data, hydrologic, precipitation, and deposition data.

Data

The following analyses utilize the pH data of collected samples from ninety sites within the GRSM. The data set includes samples collected roughly quarterly from October, 1993 to November, 2001. The independent variables used in the modeling process are listed in table 4-1. The quarterly data for 2002 became available in the spring of 2003 and was used to evaluate the predictive ability of the models developed.

Methods of Analysis

The pH models developed using the stepwise multiple linear regression procedures discussed in the methods of analysis section of chapter 4 also apply in this chapter, but slightly different evaluative procedures were used to select the best models. Often in time series modeling, a holdout data set is used to evaluate a model's ability to predict future values. A holdout R-square value is calculated for the holdout period and

the model with the highest holdout R-square value is often the best predictive model. The quarterly data for the year 2002 was used to calculate a holdout R-square value for each model obtained during the stepwise multiple linear regression process. The stepwise regression procedure enters one independent variable into the model each step to produce an overall statistically significant model that also statistically significantly improves the fit over the previous step model and also maintains all coefficients being significant at a p-value of 0.05. The final step in stepwise regression generally produces the most complex model (greatest number of independent variables) with the highest R-square value, however, the most complex models, more often than not, are not the best forecasting models. Therefore, a holdout R-square value was calculated for each step model in order to find the maximum holdout R-square value and this model was chosen as the best forecasting model if all other regression assumptions were satisfied. This procedure was used to find the best temporal trend forecasting model for the stepwise regression that includes sampling sites from all elevation classes within the GRSM.

From chapter 4, the pH modeling showed statistically significant decreasing time trends for elevation classes 2 through 6 (1000 to 3500 feet). The models for these elevation classes were quite similar and the coefficients for the time component were all of the same order of magnitude. Therefore, the data for these elevation classes were combined to form a much larger data set, which increases the statistical power of this analysis. Also, this elevation range contains a majority of the streams currently suitable to support fisheries. The stepwise procedures described in chapter 4 were performed on this data set. Also, the holdout R-square values for each step model were calculated in

order to find the best forecasting model.

The method employed by Harwell (2001) was also performed on data from elevation classes 2 through 6. Harwell's method incorporates sine and cosine functions to model the seasonal oscillations in pH and a time component which corresponds to the cumulative Julian date as measured from January 1st, 1900. The dependent pH variable was normalized by dividing each actual pH value obtained by the median pH value for that particular sampling site in order to account for the variability in pH between different sampling sites. The model takes the following form:

$$\text{normalized pH} = a + b * \cos \theta + c * \sin \theta + d * t$$

where theta equals 2 times the fraction of year at the time of sample collection and t equals cumulative Julian date.

Results and Discussion

Table 5-1 presents the modeling results for all elevation classes using pH rather than normalized pH as the dependent variable. The first model is the full model obtained in chapter 4. The fit R-square for this model is a very respectable 0.706, but the model's ability to predict the 2002 values is no where near as good as the fit would indicate as evidenced by a holdout R-square of 0.147. The second model is a reduced model that excludes two of the independent variables from the full model. The fit R-square is only slightly reduced from the full model at a value 0.692, but the holdout R-square is improved to a value of 0.236, thus supporting the principle of parsimony in time series modeling. Figure 5-1 is a scatter plot of the actual versus predicted pH values for the holdout data set. Table 5-2 lists the minimum, maximum, and median pH values for each

Table 5-1. Model results for all elevation classes

Constituent	Model	Adjusted r^2	Model p	Adjusted r^2 (2002 data)
pH Full Model	$9.10 + (4.08E-02 * \% \text{ limestone}) + (-1.47E-02 * \text{avg. basin slope in } \%) + (-3.64E-04 * \text{Little River flow in cfs}) + (-7.23E-04 * \text{elevation in meters}) + (-4.38E-05 * \text{cumulative julian date}) + (-8.90E-02 * \cosine \theta) + (-6.03E-02 * \text{closest precipitation (5) in inches})$	0.706	0.000	0.147
pH Reduced Model Maximizing r^2 holdout	$8.68 + (4.27E-02 * \% \text{ limestone}) + (-1.51E-02 * \text{avg. basin slope in } \%) + (-4.51E-04 * \text{Little River flow in cfs}) + (-7.05E-04 * \text{elevation in meters}) + (-3.11E-05 * \text{cumulative julian date})$	0.692	0.000	0.236

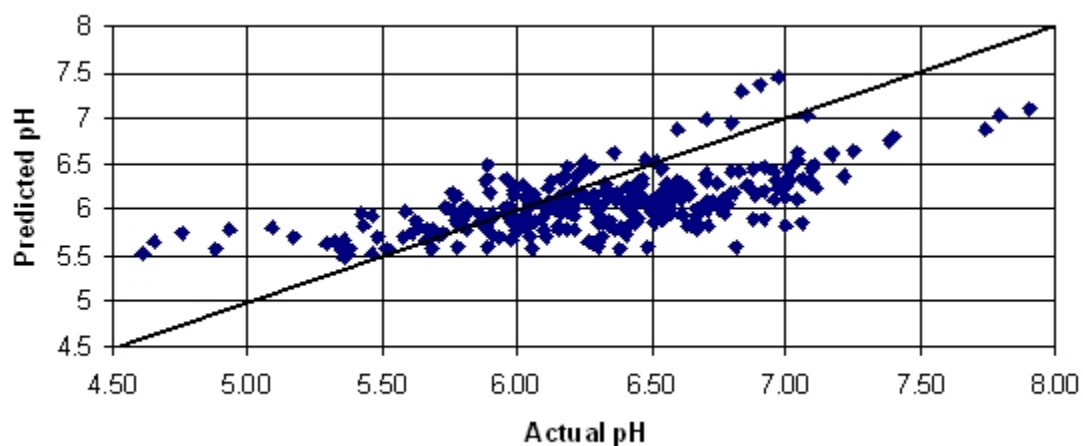


Figure 5-1. Actual versus predicted pH values for all elevation classes with a line indicating when actual pH equals predicted pH (2002 data)

Table 5-2. Time to significant pH values for all elevation classes

Elevation Class	Elevation in meters (feet)	Median pH	Minimum	Maximum	Decrease in pH per year	Time to Median pH 6.0 (yrs)	Time to Median pH 5.0 (yrs)
2	305-457 (1000-1500)	6.58	5.93	7.37	0.0114	51.1	139.2
3	457-610 (1500-2000)	6.4	5.77	7.76	0.0114	35.2	123.3
4	610-762 (2000-2500)	6.28	5.45	6.96	0.0114	24.7	112.8
5	762-914 (2500-3000)	6.31	5.26	6.8	0.0114	27.3	115.4
6	914-1067 (3000-3500)	6.16	5.2	6.73	0.0114	14.1	102.2
7	1067-1219 (3500-4000)	6.24	5.46	6.9	0.0114	21.1	109.2
8	1219-1372 (4000-4500)	5.95	5.11	6.6	0.0114	NA	83.7
9	1372-1524 (4500-5000)	6.04	4.66	6.71	0.0114	NA	91.6
10	1524-1676 (5000-5500)	5.78	4.77	6.48	0.0114	NA	68.7
11	> 1676 (> 5500)	5.11	4.65	6.21	0.0114	NA	9.7

elevation class and the decrease in pH per year as found in the best forecasting model assuming that the other independent variables remain constant. The table also includes the time in years it would take to reach median pH values below which significantly affect trout species (refer to table 2-1). If the decreasing trends in pH that the model predicts continue, all of the elevation classes could reach median pH values where detrimental effects to trout begin within about fifty years.

Table 5-3 presents the modeling results for elevation classes 2 through 6. The first model is the full model obtained through stepwise multiple linear regression procedures. The model produced a fit R-square value of 0.678 and a holdout R-square of 0.323. Maximizing the holdout R-square value produced a much simpler model (the second model in table 5-3), reducing the independent variables from eleven to five. The fit R-square value was only slightly reduced to a value of 0.650, while the holdout R-square essentially remained the same. Following the principle of parsimony, the simpler model was chosen as the best forecasting model. The third model in table 5-3 is the multiple regression modeling normalized pH. The model produced a fit R-square on normalized pH of only 0.144 and a holdout R-square value of -0.172. However, using the median sampling site pH values to convert the normalized pH values back to actual values and then calculating the R-square values produced much better results. The fit R-square value was found to be 0.751 and the holdout R-square was 0.547. Figure 5-2 is a scatter plot of the actual versus predicted pH values for the reduced prediction model and figure 5-3 is the same scatter plot for the normalized pH model.

Table 5-4 lists the minimum, maximum, and median pH values for each elevation

Table 5-3. Model results for elevation classes 2-6

Constituent	Model	Adjusted r ²	Model p	Adjusted r ² (2002 data)
pH Full Model	8.99 + (-2.29E-02*avg. basin slope in %) + (6.55E-02*stream order) + (3.37E-02*% limestone) + (-4.58E-05*cumulative julian date) + (-9.73E-02*closest precipitation (1) in inches) + (-2.02E-04*elevation in meters) + (-9.72E-02*closest precipitation (2) in inches) + (-5.50E-02*sine theta) + (-4.99E-02*cosine theta) + (-1.03E-01*closest precipitation (0) in inches) + (-3.51E-02*closest precipitation (5) in inches)	0.678	0.000	0.323
pH Reduced Model Maximizing r² holdout	8.90 + (-2.45E-02*avg. basin slope in %) + (9.46E-02*stream order) + (-3.80E-04*Little River flow in cfs) + (3.35E-02*% limestone) + (-4.70E-05*cumulative julian date)	0.650	0.000	0.322
Normalized pH	1.08 + (-1.21E-02*sine theta) + (-1.12E-02*cosine theta) + (-2.34E-06*cumulative julian date)	0.144	0.000	-0.172
		0.751*		0.547*

* R-square values calculated by converting predicted normalized pH values into actual predicted pH values using median site pH values

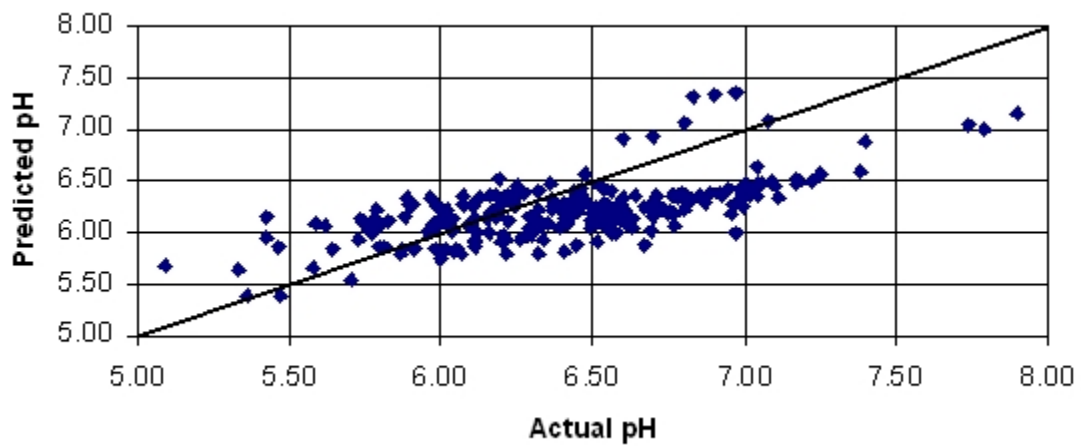


Figure 5-2. Actual versus predicted pH values for elevation classes 2-6 (reduced prediction model) with a line indicating when actual pH equals predicted pH (2002 data)

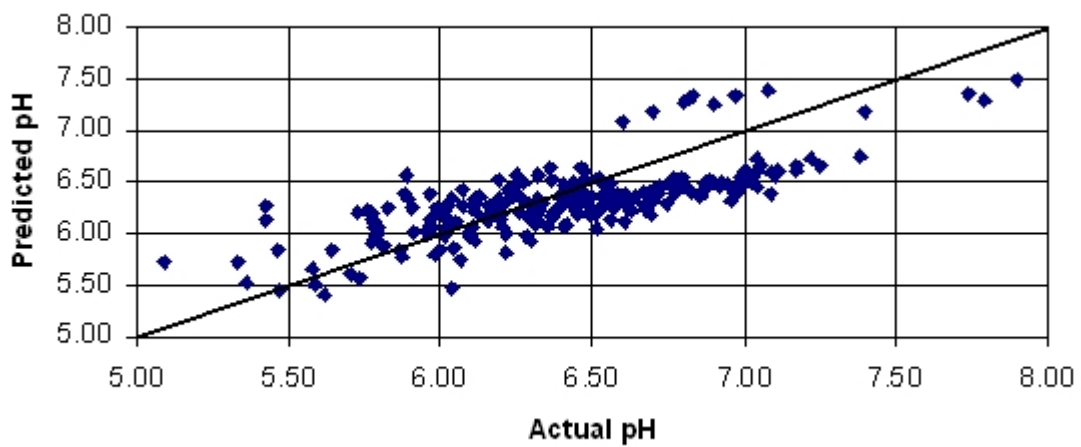


Figure 5-3. Actual versus predicted pH values for elevation classes 2-6 (normalized pH model) with a line indicating when actual pH equals predicted pH (2002 data)

Table 5-4. Time to significant pH values for elevation classes 2-6

Elevation Class	Elevation in meters (feet)	Median pH	Minimum	Maximum	Normalized pH Prediction Model				Reduced pH Prediction Model		
					Decrease in Norm pH per year	Decrease in Median pH per year	Time to Median pH 6.0 (yrs)	Time to Median pH 5.0 (yrs)	Decrease in Median pH per year	Time to Median pH 6.0 (yrs)	Time to Median pH 5.0 (yrs)
2	305-457 (1000-1500)	6.58	5.93	7.37	-0.00086	-0.005631	103.0	280.6	-0.017042	34.0	92.7
3	457-610 (1500-2000)	6.40	5.77	7.76	-0.00086	-0.005477	73.0	255.6	-0.017042	23.5	82.1
4	610-762 (2000-2500)	6.28	5.45	6.96	-0.00086	-0.005374	52.1	238.2	-0.017042	16.4	75.1
5	762-914 (2500-3000)	6.31	5.26	6.80	-0.00086	-0.005400	57.4	242.6	-0.017042	18.2	76.9
6	914-1067 (3000-3500)	6.16	5.2	6.73	-0.00086	-0.005272	30.4	220.0	-0.017042	9.4	68.1

class (2 through 6) and the decrease in pH per year as found in the normalized pH model and the reduced forecasting model assuming that the other independent variables remain constant. The table also includes the time in years it would take to reach median pH values below which significantly affect trout species (refer to table 2-1). One can see that the normalized pH model is quite a bit more conservative than the reduced model. The reduced model predicts a three times greater decrease in pH per year than the normalized pH model. If the decreasing trends in pH that the reduced model predicts continue, all five of the elevation classes could reach median pH values where detrimental effects to trout begin within thirty-four years. Table 5-5 contains the modeling results for each sampling site within elevation classes 2 through 6. The table is sorted in ascending order of the number of years to reach significant pH values. One can see that about 55% of the sites below an elevation of 3500 feet either already have median pH values less than 6.0 or will reach pH 6.0 within the next 25 years if the trends predicted by the reduced model continue.

Figure 5-4 is a map, showing the time in years it takes for a particular sampling site to reach a pH value less than 6.0.

Conclusions

The following observations and conclusions were made from the results presented earlier in this chapter:

1. The regression modeling of pH revealed statistically significant decreasing trends with time.
2. The models using hydrologic data and basin characteristics along with

Table 5-5. Time trend results for elevation classes 2-6 (1000-3500 ft)

Site ID	Elevation (ft)	Elevation (m)	Elevation Class	Median pH	Decrease in Norm pH per year	Normalized pH Prediction Model			Reduced pH Prediction Model*		
						Decrease in Median pH per year	Time to pH 6.0 (years)	Time to pH 5.0 (years)	Decrease in Median pH per year	Time to pH 6.0 (years)	Time to pH 5.0 (years)
138	3470	1058	6	5.53	-0.000856	-0.00473	NA	112.0	-0.017042	NA	31.1
45	3200	975	6	5.57	-0.000856	-0.00476	NA	119.2	-0.017042	NA	33.3
46	2750	838	5	5.77	-0.000856	-0.00494	NA	156.1	-0.017042	NA	45.2
137	2750	838	5	5.88	-0.000856	-0.00503	NA	175.0	-0.017042	NA	51.7
43	2340	713	4	5.89	-0.000856	-0.00504	NA	176.6	-0.017042	NA	52.2
47	2400	732	4	5.92	-0.000856	-0.00507	NA	181.6	-0.017042	NA	54.0
107	3040	927	6	6.04	-0.000856	-0.00517	8.2	201.6	-0.017042	2.5	61.2
213	3340	1018	6	6.11	-0.000856	-0.00523	20.7	212.0	-0.017042	6.3	65.0
192	3200	975	6	6.11	-0.000856	-0.00523	21.0	212.3	-0.017042	6.5	65.1
191	3200	975	6	6.12	-0.000856	-0.00523	22.4	213.4	-0.017042	6.9	65.5
200	3320	1012	6	6.13	-0.000856	-0.00524	24.0	214.8	-0.017042	7.4	66.1
492	2730	832	5	6.15	-0.000856	-0.00527	29.1	219.0	-0.017042	9.0	67.7
472	2200	671	4	6.17	-0.000856	-0.00528	32.6	221.9	-0.017042	10.1	68.8
71	3400	1036	6	6.19	-0.000856	-0.00530	35.8	224.6	-0.017042	11.1	69.8
184	2830	863	5	6.20	-0.000856	-0.00530	37.3	225.9	-0.017042	11.6	70.3
1	2200	671	4	6.24	-0.000856	-0.00534	44.8	232.1	-0.017042	14.0	72.7
190	2120	646	4	6.24	-0.000856	-0.00534	44.9	232.2	-0.017042	14.1	72.8
209	2700	823	5	6.24	-0.000856	-0.00534	45.3	232.5	-0.017042	14.2	72.9
49	1670	509	3	6.26	-0.000856	-0.00535	47.9	234.7	-0.017042	15.1	73.7
66	2680	817	5	6.27	-0.000856	-0.00536	49.8	236.2	-0.017042	15.7	74.3
114	2510	765	5	6.28	-0.000856	-0.00537	51.2	237.4	-0.017042	16.1	74.8
214	3440	1049	6	6.29	-0.000856	-0.00538	53.7	239.5	-0.017042	17.0	75.6
474	2400	732	4	6.30	-0.000856	-0.00539	56.0	241.4	-0.017042	17.7	76.4
475	2950	899	5	6.31	-0.000856	-0.00540	57.4	242.6	-0.017042	18.2	76.9
73	3360	1024	6	6.33	-0.000856	-0.00541	60.2	244.9	-0.017042	19.1	77.8
50	1665	507	3	6.33	-0.000856	-0.00542	60.9	245.5	-0.017042	19.4	78.0
194	1700	518	3	6.33	-0.000856	-0.00542	60.9	245.5	-0.017042	19.4	78.0
4	2080	634	4	6.33	-0.000856	-0.00542	61.7	246.2	-0.017042	19.6	78.3
186	1965	599	3	6.36	-0.000856	-0.00544	65.4	249.2	-0.017042	20.9	79.5
215	3380	1030	6	6.36	-0.000856	-0.00545	66.9	250.5	-0.017042	21.4	80.1
193	1920	585	3	6.39	-0.000856	-0.00546	70.5	253.5	-0.017042	22.6	81.3
210	2740	835	5	6.39	-0.000856	-0.00547	70.8	253.8	-0.017042	22.7	81.4
52	1350	411	2	6.39	-0.000856	-0.00547	71.0	253.9	-0.017042	22.8	81.4
488	1790	546	3	6.40	-0.000856	-0.00547	72.3	255.0	-0.017042	23.2	81.9

Table 5-5 (cont.)

Site ID	Elevation	Elevation	Elevation	Median	Decrease in	Normalized pH Prediction Model			Reduced pH Prediction Model*		
						Decrease in	Time to pH	Time to pH	Decrease in	Time to	Time to
127	2980	908	5	6.40	-0.000856	-0.00548	73.7	256.2	-0.017042	23.7	82.4
484	2475	754	4	6.41	-0.000856	-0.00548	74.1	256.5	-0.017042	23.8	82.5
143	3280	1000	6	6.41	-0.000856	-0.00549	74.7	257.0	-0.017042	24.1	82.7
34	1960	597	3	6.43	-0.000856	-0.00550	78.1	259.9	-0.017042	25.2	83.9
268	2185	666	4	6.43	-0.000856	-0.00550	78.1	259.9	-0.017042	25.2	83.9
30	1430	436	2	6.44	-0.000856	-0.00551	79.5	261.0	-0.017042	25.7	84.4
144	2990	911	5	6.44	-0.000856	-0.00552	80.6	261.9	-0.017042	26.1	84.8
142	3300	1006	6	6.46	-0.000856	-0.00553	83.2	264.1	-0.017042	27.0	85.7
479	1740	530	3	6.46	-0.000856	-0.00553	83.7	264.5	-0.017042	27.2	85.8
493	2840	866	5	6.48	-0.000856	-0.00554	86.1	266.5	-0.017042	28.0	86.7
311	2155	657	4	6.48	-0.000856	-0.00555	86.6	266.9	-0.017042	28.2	86.8
481	2540	774	5	6.49	-0.000856	-0.00555	87.4	267.6	-0.017042	28.5	87.1
482	2540	774	5	6.49	-0.000856	-0.00555	87.4	267.6	-0.017042	28.5	87.1
485	2860	872	5	6.49	-0.000856	-0.00555	87.4	267.6	-0.017042	28.5	87.1
310	2240	683	4	6.49	-0.000856	-0.00555	87.6	267.8	-0.017042	28.5	87.2
3	1675	511	3	6.50	-0.000856	-0.00556	89.1	269.0	-0.017042	29.0	87.7
20	1700	518	3	6.50	-0.000856	-0.00556	90.2	269.9	-0.017042	29.5	88.1
480	2185	666	4	6.51	-0.000856	-0.00557	90.7	270.4	-0.017042	29.6	88.3
483	2320	707	4	6.51	-0.000856	-0.00557	92.0	271.5	-0.017042	30.1	88.8
266	2015	614	4	6.52	-0.000856	-0.00558	93.0	272.3	-0.017042	30.5	89.1
150	2620	799	5	6.53	-0.000856	-0.00559	95.5	274.3	-0.017042	31.3	90.0
149	2550	777	5	6.55	-0.000856	-0.00561	98.1	276.5	-0.017042	32.3	91.0
293	2755	840	5	6.56	-0.000856	-0.00561	98.9	277.2	-0.017042	32.6	91.2
23	1150	351	2	6.56	-0.000856	-0.00561	99.8	277.9	-0.017042	32.9	91.5
147	2460	750	4	6.60	-0.000856	-0.00565	106.7	283.7	-0.017042	35.4	94.1
14	1140	347	2	6.61	-0.000856	-0.00566	107.7	284.5	-0.017042	35.7	94.4
13	1100	335	2	6.61	-0.000856	-0.00566	107.8	284.6	-0.017042	35.8	94.5
173	1715	523	3	6.66	-0.000856	-0.00570	116.1	291.5	-0.017042	38.8	97.5
148	2475	754	4	6.67	-0.000856	-0.00571	117.5	292.7	-0.017042	39.4	98.1
24	1150	351	2	6.69	-0.000856	-0.00573	121.1	295.7	-0.017042	40.7	99.4
156	1110	338	2	7.24	-0.000856	-0.00620	200.1	361.5	-0.017042	72.8	131.4
174	1715	523	3	7.40	-0.000856	-0.00633	221.1	379.0	-0.017042	82.1	140.8
489	1710	521	3	7.43	-0.000856	-0.00636	224.9	382.2	-0.017042	83.9	142.6
* Assumes other predictor variables in model remain constant.											

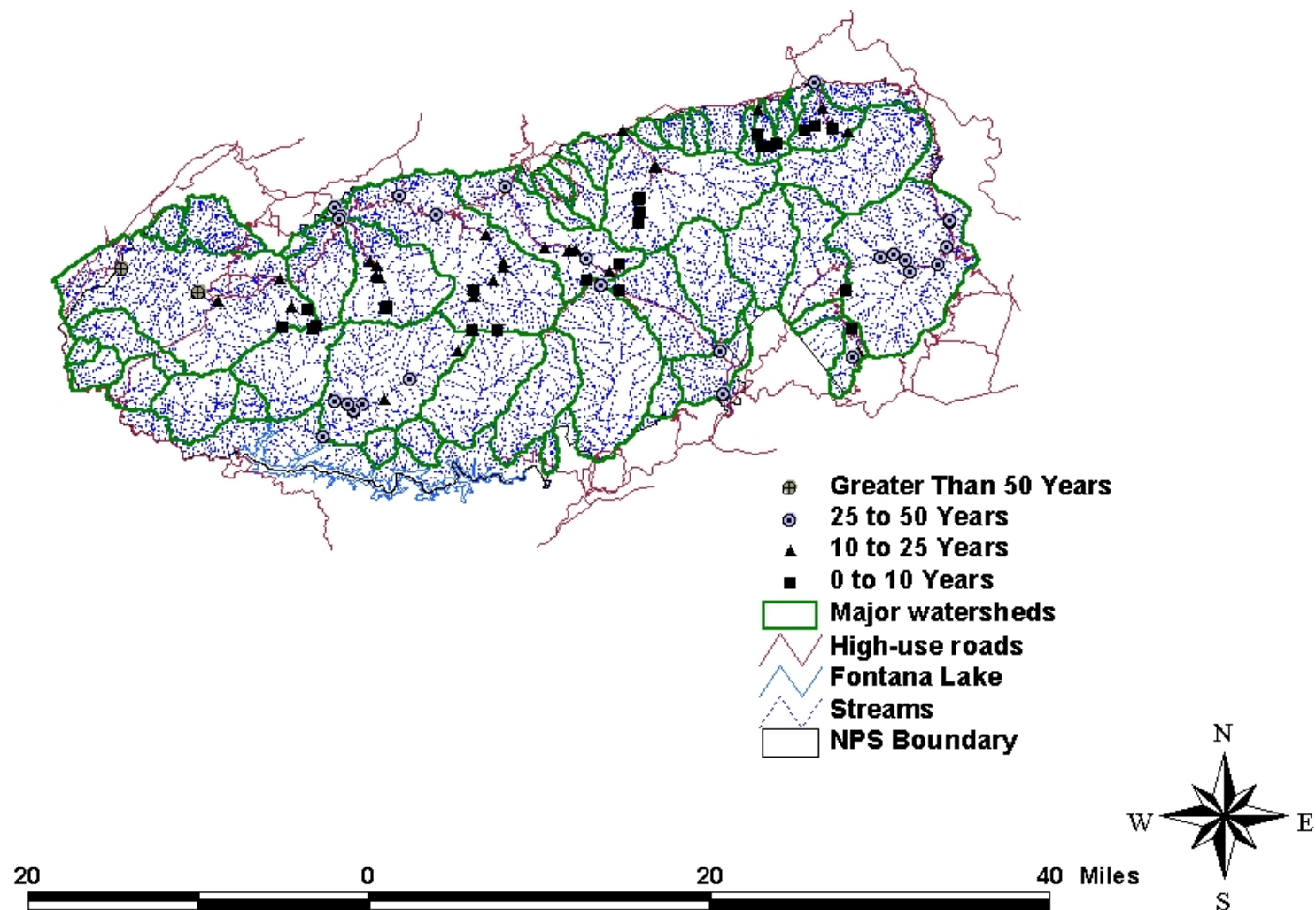


Figure 5-4. Map of the time it takes for a particular sampling site to reach a pH less than 6.0

time produced models explaining around 70% of the variability in pH, which were higher than the normalized pH models' R-square values developed by Harwell (2001).

3. The models produced R-square values of about 0.7 on the training period (1993-2001), but did not fair nearly as well on the holdout period (2002), which produced R-square values in the 0.24 to 0.33 range. Therefore, the models can indicate what factors influence stream water pH well, but their predictive capabilities are somewhat limited.
4. The pH model for all elevation classes shows that if the time trends continue the median pH values will fall below 6.0 in about 50 years. A pH value of 6.0 is the upper threshold below which adverse effects on trout species begin.
5. The pH model for elevation classes two through six indicates that median pH values for those elevation classes will reach 6.0 in less than about 34 years. Over half of the sampling sites in elevation classes two through six will reach pH 6.0 in less than 25 years.
6. Continued decreasing trends in pH could seriously affect the fisheries of the GRSM.

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Vita

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