Project Report on the Cooperative Project between The US Forest Service, VA Department of Game and Inland Fisheries and James Madison University

St. Mary's Acid Mitigation Project: Is it time for another dose of medicine?

Nathan C. Williams
Daniel M. Downey
James Madison University
Chemistry Department
MSC 4501
Harrisonburg, Virginia 22807

Abstract

Water samples were collected at various time intervals from 1999-2010 from the streams of the St. Mary's Wilderness, Augusta County, Virginia. The samples were analyzed for pH, acid neutralizing capacity (ANC), base metal cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), major acid anions (Cl^{-}, SO_4^{2-}, NO_3^{-}) and aluminum (Al_T) concentrations. The resultant chemical data supplemented biological data for fish, amphibians and aquatic insects in an acid precipitation mitigation project. On March 20, 1999 and November 3 & 5, 2005 the St. Mary's River and six of its tributaries were treated with 140 and 230 tons of limestone, respectively, (>99% $CaCO_3$) delivered by helicopter. Twenty-two samples were taken on a quarterly basis at locations in the watershed both upstream and downstream of the liming sites from January 1999 until April 2005. In addition, three sample locations (one at St. Mary's and two at control streams) were monitored weekly. Several samples were collected 2005-2010. The pH, ANC, calcium/hydronium ratios and calcium/magnesium ratios increased as a result of the limestone treatment. For the six year period following the first liming (1999-2005) key water chemistry parameters for St. Mary's River increased with pre-liming averages to post-liming averages as follows: pH 5.36 ± 0.22 to 6.05 ± 0.51; ANC -9.1 ± 7.9 to 23.8 ± 29.3 μeq/L; calcium/hydronium ratios 5.1 ± 2.9 to 83.5 ± 101; calcium/magnesium ratios 0.7 ± 0.03 to 1.6 ± 0.6. As a result of the increased pH, aluminum concentrations decreased from 78 ± 32 to 52 ± 40 ppb during this period. The other strong acid anions and base metal cations have not significantly changed. Limited water quality data were obtained post 2005 due to budget limitations. Recent data were assured to provide an estimate on how soon re-liming will be necessary. From these data and the model for limestone consumption we recommend that a third limestone treatment be implemented by 2012.

Background

St. Mary's River is located in Augusta Co., Virginia in the George Washington National Forest. It has historically been viewed by anglers as one of the better trout streams in Virginia because it supported both an abundance and diversity of coldwater fish. However, by the 1980's atmospheric acid deposition was taking a toll with loss of biomass and species. By the late 1990's it was decided to pursue a management strategy of mitigative liming to restore pH and ANC lost to acidification. It was recognized from the outset that mitigative liming provides temporary benefits and would eventually need to be repeated. Thus extensive water quality monitoring was conducted before and after liming to provide data used to evaluate water chemistry changes and predict the optimum time for reliming.

In 1998 we (JMU Chemistry, Dept. Downey Lab) estimated that 125 tons of limestone sand introduced into the upper reaches of St. Mary's River and its tributaries would provide five years treatment to offset the effects of acid deposition. This estimate was based on existing stream water chemistry, annual rainfall, stream discharge and acid loading[1, 2]. After reviewing the data from the first liming, in 2004 it was proposed that 200 tons of limestone was needed for a five to seven year treatment[3]. The limestone was distributed to six locations within the Wilderness by helicopter in March 1999 and seven locations in November 2005 (Table I). The stream sites with greater discharge and lower pH received more limestone than those of lower discharge and higher pH. A total of 140 and 230 tons were actually distributed in 1999 and in

2005, respectively. At all the liming sites limestone was placed far enough upstream to treat the maximum length of each stream, yet not at sites of intermittent flow. Stream gradient was generally 2-5%. The limestone placed at these sites moved downstream due to the flow of the stream water and incorporated into the substrate to form treatment zones of 150-250 meters. As found for other stream liming projects we have designed, it was intended that the limestone would slowly dissolve as stream water flowed over the substrate to provide a "timed release" treatment. More than 10 miles of stream were thus treated within the Wilderness Area.

Table I: Limestone sand allocations in the St. Mary's Wilderness.

Site	1999 liming	2005 liming
Upper St. Mary's	50	75
Hogback Creek	25	36
Chimney Branch	15	26
Bear Branch	20	30
Mine Bank Creek	15	24
Sugartree Branch	15	23
Northern tributary	0	16
Total	140	230

The limestone used to treat St. Mary's River and its tributaries was high grade (>99%) calcium carbonate mined from a quarry in the Shenandoah Valley near Middletown, Virginia. As expected from prior work[2], dissolution was slow as the stream water contacted the limestone in the substrate, and freed both Ca^{2+} and carbonate, CO_3^{2-}, ions into the water column. The principal buffer provided by the limestone dissolution was bicarbonate ion HCO_3^{2-}, which was formed by the following reactions:

$$CaCO_3 + H_2O \leftrightharpoons Ca^{2+} (aq) + CO_3^{2-} (aq)$$

$$CO_2 + H_2O \leftrightharpoons H_2CO_3 (aq)$$

$$H_2CO_3 (aq) + CO_3^{2-} (aq) \leftrightharpoons 2\ HCO_3^{-} (aq)$$

Streams in the St. Mary's Wilderness have experienced high acidity levels for two reasons. First, rainfall in the region shows elevated acid levels due to anthropogenic atmospheric acid. This acid has been deposited in the watershed by rainfall, snow and other precipitation (Table II). Second, the bedrock geology of the watershed is almost entirely Antietam Formation quartzite, a low solubility silicilastic rock that provides little natural carbonate. Hence the streams that drain the watershed have little natural buffer to neutralize the acid introduced from the atmosphere. Low pH water has a detrimental effect on aquatic biota that have evolved in circumneutral waters. The effect is in part due to ionic imbalance and hydronium ion influence on cells of affected fish and other species, but also low pH water mobilizes aluminum from soil and minerals contacted by the water.

Aluminum is one of the most abundant elements in the earth's crust. Its mineral forms are not very soluble at "normal" pH levels, but solubility increases as pH decreases. In acidic water, aluminum minerals dissolve to form Al^{3+}, AlO^{+} and other aluminum species. The dissolved aluminum enters the gills of fish where it precipitates due to the alkaline environment of the fish tissue. The precipitate causes irritation, stress and may result in mortality[4]. The direct benefit of limestone treatment is that the stream pH is raised by the added bicarbonate ion (HCO_3^-) neutralizing the acid (H^+). Once the pH is increased, aluminum species are no longer stable in the stream water, are precipitated and returned to the mineral form.

Table II. Comparison of wet precipitation for three years preceding 1999 and 2005 limings and St. Mary's average water chemistry (1999-2005). Precipitation values calculated from monthly average data collected at Charlottesville Station, VA00 (National Acid Deposition Program, 2010). The lower SM values are for the ten monitored sites downstream of treatment in St. Mary's River. ND = none detected. NM = not measured. All concentrations are given as µeq/L except pH (standard units) and Al_T (ppb).

Parameter	Precipitation 01-03	Precipitation 06-08	St. Mary's Upper	SM Lower (Pre 1999 liming)	SM Lower (Post 1999 liming)	SM Lower (4/10/10)
pH	4.44 ± 0.10	4.58 ± 0.10	4.88 ± 0.20	5.36 ± 0.22	6.05 ± 0.51	5.12 ± 0.27
ANC	NM	NM	-13.9 ± 7.8	-9.1 ± 7.9	23.8 ± 29.3	-4.0 ± 5.2
Ca^{2+}	3.3 ± 0.7	4.2 ± 1.0	10.1 ± 3.0	17.4 ± 2.6	39.5 ± 22.5	39.1 ± 5.7
Mg^{2+}	1.2 ± 0.3	1.8 ± 0.6	16.3 ± 2.1	23.4 ± 2.9	23.4 ± 3.7	33.1 ± 5.2
Na^{+}	3.8 ± 0.8	5.2 ± 2.9	12.8 ± 2.9	10.5 ± 4.0	14.9 ± 3.4	17.0 ± 1.5
K^{+}	0.4 ± 0.1	0.5 ± 0.2	9.6 ± 2.7	10.4 ± 2.7	14.2 ± 2.7	12.2 ± 1.6
H^{+}	36.3 ± 8.1	26.5 ± 5.9	16.3 ± 4.4	10.5 ± 3.3	0.26 ± 0.12	8.5 ± 5.3
NH_4^{+}	13.4 ± 2.8	12.6 ± 2.2	ND	ND	ND	ND
Cl^{-}	5.1 ± 0.9	6.4 ± 3.2	16.9 ± 5.7	13.5 ± 5.1	17.2 ± 3.3	16.5 ± 2.0
NO_3^{-}	19.7 ± 5.2	15.1 ± 2.7	1.6 ± 1.0	8.0 ± 6.3	2.4 ± 2.4	0.3 ± 0.3
SO_4^{2-}	35.8 ± 7.6	28.4 ± 6.1	59.2 ± 8.8	72.0 ± 10.2	56.7 ± 7.6	60.9 ± 2.3
Al_T	NM	NM	177 ± 74	78. ± 32	52. ± 40.	63. ± 37.
Ca^{2+} / H^{+}	0.09 ± 0.01	0.16 ± 0.03	0.94 ± 0.7	5.1 ± 2.9	83.5 ± 101.	6.6 ± 5.4
Ca^{2+} / Mg^{2+}	2.8 ± 0.5	2.3 ± 0.8	0.6 ± 0.2	0.7 ± 0.03	1.6 ± 0.6	1.2 ± 0.09
Precipitation (cm)	120.9 ± 53.7	103.4 ± 16.5	NM	NM	NM	NM

Not only is the bicarbonate ion important in the restoration of an acid degraded stream as described above, but calcium ion (Ca^{2+}) also plays an important role. Calcium ion is beneficial to aquatic life as it is an essential nutrient and offsets the effect of toxic aluminum on fish and other aquatic life. The calcium from the limestone helps prevent aluminum adsorption by competing for cation exchange sites in fish gills.

Water chemistry data were collected for the project to answer three primary questions. First, were the pH and other water quality parameters changed within the stream system of St. Mary's Wilderness as a result of liming; second, was the mass of introduced limestone adequate for an extended period of treatment and third, how long would the treatment last (when would the system need to be re-limed). To answer these questions water chemistry data were generated from stream samples collected throughout the Wilderness at scheduled intervals before / after and upstream / downstream of liming sites. Extensive data were collected in the first six years of the project (1999-2005). Since then and following the second liming (2005-2010) limited water quality data have been obtained due to budget limitations. The purpose of collecting recent data was to evaluate water chemistry in the St. Mary's River five years following the second liming. Acid mitigation in a trout stream may be viewed as similar to treatment of acid indigestion in a human being. As with treatment of humans, the "medication" resultant from liming must be repeated until such time as the acid source is eliminated. These data are reported below to answer the question: Is it time for another dose of medicine?

Monitoring Results

Sampling Schedule

Water chemistry monitoring of the St. Mary's River by JMU began in January 1999, three months before the date of the first liming treatment. Twenty-two sites (Table III and Table IV;

Figure 1) were sampled for water quality throughout the Wilderness on a quarterly basis, including a site (SM 1) located at the lower boundary where the stream exits the Wilderness Area.

Table III: JMU water chemistry sampling sites in The St. Mary's Wilderness.

Site ID	Location	Distance from liming site (km)
SM 1	Lowest elevation site at the Wilderness boundary	8.14
SM 2	0.5 mi upstream of SM 1	7.48
SM 3	Downstream of confluence of Sugartree Branch	5.67
SM 4	Upstream of confluence of Sugartree Branch	5.31
SM 5	Midway between falls	3.57
SM 6	Downstream of confluence of Mine Bank Run	2.81
SM 7	At old mine site near Bear Branch	2.48
SM 8	Downstream of confluence of Hogback Run	2.02
SM 9	Downstream of confluence of Chimney Branch Run	1.19
SM 10	At trail ford downstream of liming site	0.62
SM 11	Upstream of liming site	-0.14

A staff gauge was placed at SM 1 for measuring stream discharge. Samples were collected and flows recorded at SM 1 once a week from the first date of liming until September 2003 to supplement the quarterly water chemistry data. Water samples, but not flow data, were collected from September 2003 to March 2005. Several samples have been collected since then. Water samples were also collected weekly at Coles Run and Spy Run throughout the project period. These two nearby streams were not treated and served as "control" streams.

Table IV: JMU water chemistry sampling sites for tributaries of The St. Mary's River.

Site ID	Location	Distance from liming site (km)
BB1	Downstream of Bear Branch liming	1.85
BB2	Upstream of Bear Branch liming	-0.02
CB1	Downstream of Chimney Branch liming	1.50
CB2	Immediately downstream of Chimney Branch liming	0.30
CB3	Upstream of Chimney Branch liming	-0.02
HC1	Downstream of Hogback Creek liming	0.30
HC2	Upstream of Hogback Creek liming	-0.02
MBC1	Downstream of Mine Bank Creek liming	1.09
MBC2	Upstream of Mine Bank Creek liming	-0.02
STC1	Downstream of Sugartree Branch liming	0.30
STC2	Upstream of Sugartree Branch liming	-0.02

Hydronium Ion Concentration (pH) and Discharge

Values for pH are measured to find the hydronium ion concentration (acid) in water. Low values indicate acidic conditions, which can cause mortality due to stress in fish and other aquatic life. For a water body managed for brook trout, pH 5.5 is considered the minimum acceptable value, with values > 6 preferred[5]. The limestone was added to raise the pH above these values from the low (pH < 5.5) values found upstream of the liming sites, and prior to liming for many downstream sites (Figure 2).

Stream discharge is the volume rate of stream flow at a given point. The rate or velocity of stream flow is dictated by gradient and resistance of the streambed. The volume of stream flow is controlled by base flow, precipitation, vegetation, springs and tributaries. The two primary, variable affecters of discharge for the St. Mary's River are precipitation and vegetation. Summer months typically show low discharge due to the transpo-evaporation process used by vegetation for cooling, transporting groundwater into the atmosphere. Discharge is reported with pH because of the effect discharge has on pH following liming (Figure 3). At some point in time following a liming treatment, substantial discharge will cause the pH to rise dramatically due to the large amount of water dislodging the pile of introduced limestone sand and spreading it downstream. When the limestone sand is spread out it will dissolve more effectively due to the increased exposed surface area. Conversely, a low discharge shortly following a liming will not raise the pH very much because of the smaller surface area of the pile and reduced contact time. For most limestone treatment we have done, it has taken from a few days to several months for the introduced limestone to spread and incorporate into the stream substrate. Once that has occurred, the 150 – 250 m "treatment zone" will slowly be consumed as the stream flows through ie. when the treatment zone has established stream pH will be higher under low flow conditions and lower under high flow conditions due to velocity and contact time.

The pH and stream discharge were recorded at SM 1 weekly (Figure 3) during the primary phase of the project. There was a lengthy period during which no data were collected between the second liming, November 2005, and April 2010. The pH values were often less than the minimum acceptable value at the sampling site prior to the introduction of limestone (Figure 3A). The average value for the period prior to the first liming was pH 5.53 ± 0.28. From the first liming until April 2005 the average pH was 6.08 ± 0.32. This is a significant improvement that has benefited the aquatic life in the stream. There was substantial flow on the day the streams were limed, but the spring and summer of 1999 were extremely dry times with discharge significantly decreasing. In September 1999, several tropical depressions provided rainfall that increased discharge (Figure 3B). At this time the limestone bed that had mostly remained immobile during the summer months distributed in the streams and pH increased dramatically to values > pH 6. During the years that followed, pH generally decreased as the limestone was consumed. Storm events generally caused short-term decreases in pH, but episodic pH dips were not as low as they were prior to liming, thus the aquatic life was generally protected from hydronium ion stress.

Unfortunately the stream discharge data ended on September 19, 2003 when runoff from Hurricane Isabel destroyed the staff gauge. It was not replaced, but weekly samples for water quality were collected until April 2005. To supplement the water quality data obtained weekly at SM 1, ten additional sites along the St. Mary's River were sampled quarterly from January 1999 to April 2005. A graph of pH versus stream reach (Figure 4) for five selected quarters shows that both before and after liming, pH gradually increases upstream to downstream due to the increases in carbonate bearing minerals in the bedrock geology at lower elevations. The higher pH values were found in September 1999 for reasons explained above. April pH values for 2004 and 2005 were close to the pre-liming values. Only three water chemistry sample sites have been collected from St. Mary's since April 2005. Two samples were collected at SM 1 (before / after) the November 2005 liming, and the quarterly set taken in April 2010. The pH value increased dramatically immediately following the 2005 liming, but returned to near pre-liming values in the most recent results. These data suggest the second limestone treatment responded similar to the first treatment. April 2010 pH values throughout the watershed (Figure 5) are provided for comparison to the pre-liming values (Figure 2). These results indicate the St. Mary's River is ready to be limed again.

Acid Neutralizing Capacity (ANC) and Calcium/Hydronium Ratio (Ca/H)

Chemically available dissolved buffer (acid neutralizing capacity, ANC) in stream water samples is determined by acid titration and reported in equivalence of $CaCO_3$. The significance of the ANC is that it shows how close the stream is to becoming acidic and unsupportive of acid intolerant aquatic life[6]. In fact, ANC is a better metric for assessing the acid base status of a natural water than pH as it is an absolute value (not logarithmic) and gives the amount of available buffer present. Another important metric, the calcium to hydronium ratio (Ca/H) value is calculated from the calcium concentration and the pH found for a water sample. Lower pH values can be tolerated by aquatic life when Ca/H ratio values are large. The Ca/H ratio is important because it indicates a level of protection for the gills of fish from aluminum absorption[7]. The target value for St. Mary's liming project are > 25 µeq/L ANC and Ca/H ratio > 2, respectively.

Weekly SM 1 results for ANC (Figure 6C) and Ca/H (Figure 6D) show the same growth and decay for the project period as pH values. The ANC values were quite low for the St. Mary's River prior to liming, often showing negative values. The pre-liming ANC average was 2.1 ± 4.7 µeq/L. The low values are the result of a lack of carbonate bearing mineral in the Antietam Formation quartzite rock that makes up most of the St. Mary's Wilderness watershed. Thus little natural buffer is available to mitigate anthropogenic acidity from the atmosphere. The post-liming ANC values increased due to the slow dissolution of the introduced limestone sand to an average 24.4 ± 11.7 µeq/L. There was an ANC decrease during the 1999 drought coincident with the pH decrease described above, but an increase above target value of 25 µeq/L (marked on the graph) followed the 1999 drought. Except for some depressions in the years that followed caused by storm events, the ANC remained near 25 µeq/L until 2003 when an extended period of low values was observed due to the unusually high flows. Although the ANC values were less than the target value during this period it is likely that the values were not as low as would have been observed had mitigative liming not been done. The similar ANC values between the 1/99, 4/04, 4/05, and 4/10 (Figure 7), along with the ANC values for pre-liming (Figure 2) and in April 2010 (Figure 5), indicate that the St. Mary's is ready to be limed again.

The Ca/H ratio was measured at 11 sites along the St. Mary's from the period prior to any treatment (1/99), a period shortly after the first liming (9/99), two periods at the end of the expected treatment lifespan (4/04 and 4/05), and the most recent sampling (4/10) (Figure 8). A generally accepted minimum value of 10 was chosen for this parameter (shown on the graph). Prior to liming, the Ca/H averaged 8.5 ± 4.8, while the average was 65.1 ± 52.0 post-liming. It is likely that Ca/H ratio would have been much less than 10 during the recent high flow periods without the mitigative liming. The similar Ca/H values between the 1/99, 4/04, 4/05, and 4/10 indicate that the St. Mary's is ready to be limed again.

Calcium / Magnesium Ratio

Calcium and magnesium ions are naturally present in stream water from dust deposition or erosion of minerals in the watershed. Both ions are essential elements for fish survival and growth. Upstream of the liming sites and pre-liming data provide calcium to magnesium ration values that are reflective of the natural abundance of these two elements in the watershed. The limestone treatment was done with material that was almost entirely $CaCO_3$, so changes in calcium concentration not complimented by similar changes in magnesium concentrations indicate water chemistry changes directly resultant from the liming. The calcium to magnesium ratio values, rather than absolute concentrations, are reported to minimize the effects of low and high discharge events on the values.

The effect of the first liming in 1999 is revealed by the marked increase calcium to magnesium ratio (Figure 9) immediately following liming. The limestone sand used for this study was high grade (>99% $CaCO_3$) and it contained essentially no magnesium, only calcium in the form of calcium carbonate. Like calcium, magnesium is a base cation and a group II metal that enters the stream water naturally from the weathering of the minerals in the soils and bedrock. Since the amount of magnesium would not have changed after liming, the calcium to magnesium ratio results from the increase in calcium concentration after liming due to limestone dissolution. The average calcium to magnesium ratio prior to liming was 0.75 ± 0.04. Following the first liming the average ratio increased to 1.34 ± 0.32 for the initial project period. The dramatic increase is due solely to limestone dissolution, not natural effects. The most recent Ca/Mg ratio values are similar to the pre-liming values (Figure 10) indicating that the treatment limestone has been depleted.

Aluminum

Aluminum is a fish toxin as described above. A total aluminum concentration level above 130 ppb is considered hazardous for aquatic life and thus was chosen as the maximum acceptable amount for this study[4]. The total aluminum concentration for the St. Mary's River was measured from the weekly samples taken at the gauging location (Figure 11E) and the quarterly aluminum values taken at the control site upstream of the limestone treatment (Figure 11F). The graphs show that aluminum was mobilized during high flow periods due to low pH and flushing in the untreated reach of the stream. Episodic short-term spikes in aluminum concentrations as well as the base flow concentrations were less than the target value downstream of limestone treatment. Aluminum concentration at site 1 averaged 39.3 ± 18.0 ppb prior to liming and 22.6 ± 19.7 ppb post-liming for the initial project period. Figure 12 shows aluminum concentration in relation to distance from the liming site.

Rainfall and Control Streams

Atmospheric acid deposition may have decreased over the ten year period of this project as shown by the weekly pH values of precipitation in the region (Figure 13). However this decrease has been too small to provide any significant increase in pH of the control streams, Spy Run and Cole's Run. These data support the conclusion that increases in pH (and other water quality parameters) in St. Mary's River and its tributaries during the initial project were due solely to the limestone introduction and unrelated to environmental changes.

Limestone Consumption Model

In the environmental assessment documentation for this project, re-liming was anticipated. The following statement was made: "One threshold that may trigger consideration of re-liming is when the pH, acid neutralizing capacity (ANC), and calcium values in April under normal flow are down to 30% of the first year water quality improvement." The year 2003 was anything but a "normal" year, but the numbers were less than 30% of the first year treatment. In fact, assessment of the time for re-liming was an integral and continuous part of water chemistry data collection for the initial project period. As an example of the liming data evaluation, the calcium decay graph is provided (Figure 14). This graph was used to assess limestone consumption and predict the need for a second treatment as follows. Calcium increases in the stream have been shown to be due solely to limestone dissolution. The graph is a plot of the difference between weekly calcium concentrations and the average background concentration versus the day number post liming. This graph fits an exponential decay plot, and gives the equation:

$$\mathbf{Y} = 35.58\ e^{-(0.001146\mathbf{x})}$$

The first 150 days of post treatment data were not used in generating this plot due to low flow conditions in the summer of 1999. After the tropical storms increased the flow in September of that year, the limestone treatment was activated. From the exponential decay plot, a consumption half-life was calculated to be 1.65 years. By using the first order kinetic decay model it was estimated that 93% of the added limestone was consumed by the second liming in November 2005. If the assumption is made that the kinetics are the same for the second liming as found for the first liming, then the 93% consumption level will be met in February 2012.

Recommendation for Third Liming

There were several reasons the mass of limestone introduced in the St. Mary's Wilderness from the first to the second liming was increased from 140 to 230 tons. The original estimate was made to provide for a five year treatment period and it was thought that the increase would extend the treatment period to seven years. In addition, more limestone was added to compensate for transportation losses, etc. Exponential curves for the two dosage amounts (Figure 15) reveal that diminishing returns occur after about three or four half-lives have passed (7 years). We estimate that about seven tons of limestone remained from the initial liming when the Wilderness streams were treated a second time. Using the decay model, we estimate that there will be about seven tons left from the second liming in 2012. If a third liming treatment is done, we believe that any additional increase in mass of limestone over the 2005 amount will not significantly extend the treatment period to merit the increased costs, transportation, labor, Wilderness closure during liming or other associated issues.

The limited water quality data collected for St. Mary's since the 2005 project period do not provide a complete picture of how the second liming affected the stream chemistry. However, if it is assumed the model developed in the initial project period (and from other liming projects) is reliable, then the lack of extensive water chemistry does not handicap evaluation for a future liming project. In fact, the results of the several water quality samples that were collected support the model's prediction for the second liming, including the marked increase in pH, ANC, Ca/H, Ca/Mg and decrease in Al observed immediately after the limestone was introduced (Figures 3A, 6C, 9G, and 11E). The extensive water chemistry data collected throughout the St. Mary's Wilderness in April 2010 (Table V) provide the most useful information for assessing the acid base status of the streams in the Wilderness. The values for April 2004 and 2005 are included for comparison. Concentration values alone are indeterminate for assessing water quality and must be qualified by stream discharge. Unfortunately no discharge data were obtained in 2010 due to the absence of a flow gauge. However, discharge can be estimated by the amount of rainfall prior to the sample date (Table VI) since the yield is fairly constant in this watershed.

Table V: Water chemistry values for all sites sampled in 2010.

Site	pH	ANC	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al_T
SM1	5.61	6.5	18.2	0.4	65.0	91.0	41.4	19.4	15.2	19
SM2	5.22	-5.3	16.2	0.2	61.7	78.9	38.7	17.1	13.6	28
SM3	5.23	-3.3	15.7	0.3	60.5	302.4	38.1	16.2	12.5	28
SM4	5.40	2.6	16.4	0.3	59.2	36.8	31.4	17.8	12.1	36
SM5	5.14	-3.3	15.6	0.4	58.8	35.6	30.8	17.2	12.3	54
SM6	5.20	-4.6	16.3	0.0	58.2	82.9	31.3	17.2	13.3	57
SM7	4.93	-7.8	14.8	0.0	61.4	34.7	30.6	15.4	11.1	78
SM8	4.81	-10.5	14.7	0.0	60.8	324.9	36.0	15.3	11.1	89
SM9	4.75	-9.8	21.5	0.9	64.3	248.3	27.8	19.2	10.9	123
SM10	4.94	-4.6	15.4	0.2	59.5	30.4	25.1	15.5	9.9	114
SM11	4.62	-28.9	12.9	0.2	71.6	9.0	12.7	13.4	3.0	290
BB1	5.86	16.3	15.4	0.2	45.8	41.3	32.8	17.9	16.5	14
CB1	5.93	21.6	15.5	0.2	60.1	215.0	34.4	18.2	19.6	18
CB2	6.21	43.1	14.4	1.8	59.4	84.3	47.4	19.3	28.4	11
CB3	5.95	15.7	13.6	5.6	60.1	45.2	44.9	18.1	26.0	6
HC1	5.40	3.3	14.8	0.7	59.7	47.5	32.2	15.5	16.3	24
MBC1	5.65	3.3	14.8	0.2	52.3	38.7	37.9	16.8	18.0	17
MBC2	5.84	15.0	15.6	0.4	34.3	307.1	28.5	16.6	19.4	19
STC1	5.80	31.4	17.5	0.3	74.0	48.5	55.1	21.9	22.0	24
STC2	4.60	-20.3	20.7	0.2	88.5	28.6	50.1	18.1	12.3	170
Swamp	4.71	-23.2	15.8	0.2	67.1	11.2	16.9	16.5	4.9	290

The discharge data collected at St. Mary's from 1999-2003 along with the historical rainfall data enabled the calculation of the discharge for April 19, 2004, April 16, 2005 and April 10, 2010. Pre-liming discharge values for the dates following February 4, 1999, March 9, 1999 and March 1, 1999, respectively, matched the post-liming dates. The first two post-liming dates were for five and six years, respectively, after the first liming. The other post-liming date was for five years after the second liming. Values for ANC, Ca/H and Ca/Mg were greater than pre-liming values for all these post-liming values, and Al was reduced, which was a goal of the liming project. Extrapolating to 2011 it may be expected that the limestone from the second liming will still be treating the stream, but with less improvement. Based on these values and the predicted limestone consumption described above, it is recommended that St. Mary's be treated with limestone a third time in the late winter of 2012 to maintain the water quality necessary for protection of aquatic life.

Table VI: Rainfall (cm) for time periods prior to selected April sampling dates five years post-liming. Rainfall recorded by precipitation station in Staunton, VA. (Data courtesy of wunderground.com).

	4/19/2004	4/16/2005	4/10/2010
3 days	0.0	0.15	0.0
1 month	11.33	9.09	6.88
3 months	24.16	21.13	12.45
6 months	60.38	44.75	36.91

Table VII: Water chemistry parameters found for SM 1 and discharge equivalent values pre-liming for five years (April 2004), six years (April 2005) and five years (April 2010) post-liming # 1 and # 2, respectively. All concentrations are in μeq/L, except pH (standard units) and Al_T (ppb).

	Five Year		Six Year		Five Year	
Parameter	4/19/2004	2/4/1999	4/16/2005	3/9/1999	4/10/2010	3/1/1999
pH	5.60	5.13	5.56	5.65	5.61	5.63
ANC	5.3	-1.6	7.3	2.8	6.5	2.1
Cl^-	16.6	14.2	16.7	17	18.2	13.6
NO_3^-	2.0	1.5	0.9	4.4	0.4	ND
SO_4^{2-}	66.7	63.4	60.3	62.6	65.0	70.
Ca^{2+}	28.5	22.1	23.9	23.9	48.3	18.8
Mg^{2+}	29.7	29.1	27.0	30.3	41.4	28.7
Na^+	21.8	11.6	14.6	10.1	19.4	9.7
K^+	18.1	13.7	12.5	14	15.2	12.5
Al_T	35	53	10	30	19	28
Ca/H	11.3	2.98	8.7	10.68	19.7	8.02
Ca/Mg	1.0	0.76	0.9	0.79	1.2	0.66

Final Thoughts

One concern that was raised in the early years of stream liming is that aluminum would mobilize as the streams became more acidic when the limestone was consumed. It was said that this increase in Al_T would cause fish mortality. The data indicate that Al_T has not increased and remains well below the toxicity level (150 ppb). Another concern was that limestone would raise the pH of wetlands in the watershed that support Swamp Pink (*Helonias bullata*) which is a federally threatened plant that requires acidic conditions for survival. Limestone was introduced in the Wilderness in such a manner and in locations to avoid areas occupied by this plant. Water chemistry values (Table V, Swamp) collected from the discharge of the largest wetland where Swamp Pink is located showed no change, as compared to the upstream, untreated control site (SM 11).

References Cited:

1. Downey, D. M., French, C. R. and Odom, M. 1994. Low Cost Limestone Treatment of Acid Sensitive Trout Streams in the Appalachian Mountains of Virginia. Water, Air and Soil Pollution. 77:49-77.
2. Hudy, M., Downey, D. M. and Bowman, D. W. 2000. Successful Restoration of an Acidified Native Brook Trout Stream through Mitigation with Limestone Sand. North American Journal of Fisheries Management. 20:453-466.
3. Internal Report, JMU to USFS, 2004.
4. Baker, J. P. and Schofield, C. L. 1982. Aluminum Toxicity to Fish in Acidic Waters. Water Air Soil Pollut. 18:289-309.
5. Brown, D. J. A. 1982. The Effect of pH and Calcium on Fish and Fisheries. Water Air Soil Pollut. 18:343-351.
6. Cosby, B. J., Ryan, P. F., Webb, J. R., Hornberger, G. M. and Galloway, J. N.: 1991. Mountains of Western Virginia. Chapter 10, in D. F. Charles (ed.), *Acid Deposition and Aquatic Ecosystems: Regional Case Studies.* Springer-Verlag, New York, NY. 297-318.
7. Brown, D. J. A. 1983. Effects of Calcium and Aluminum Concentrations on the Survival of Brown Trout *(Salmo trutta)* at Low pH. Bulletin of Environmental Contamination Toxicology. 30:582-587.

List of Figures

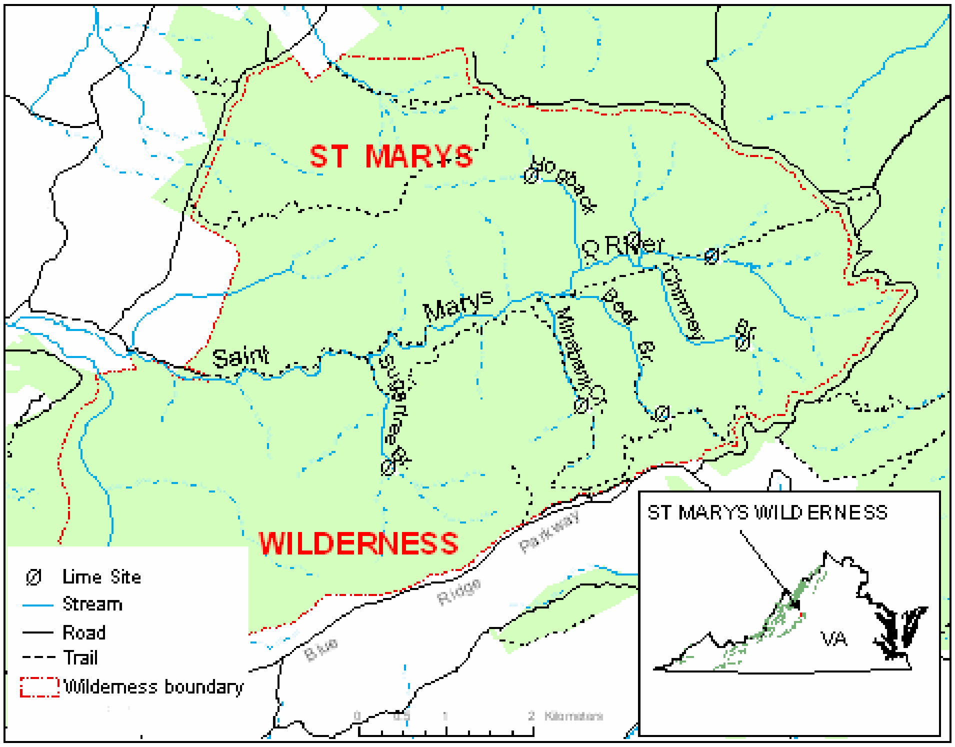

Figure 1: Map of St. Mary's Wilderness showing the St. Mary's River and its major tributaries. Approximate locations of 2005 liming sites are indicated (ø). (Map courtesy of United States Forest Service).

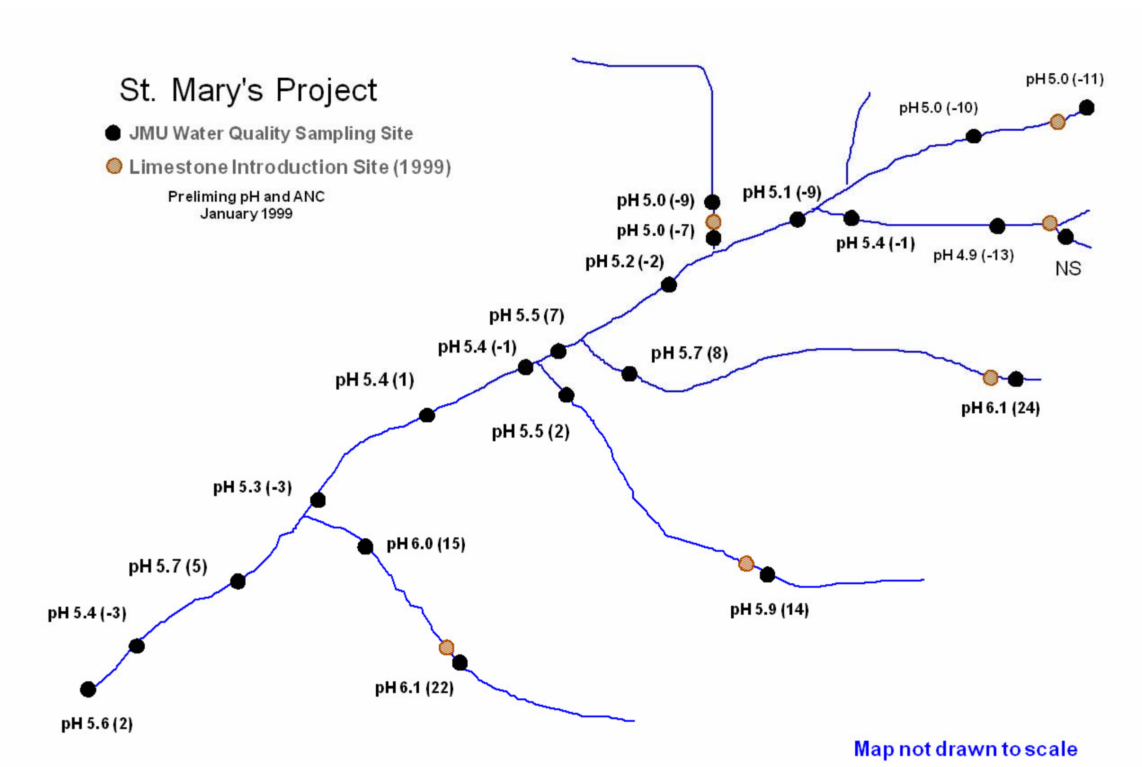

Figure 2: Map of St. Mary's Wilderness with pH and ANC values at sampled sites in January 1999 prior to the introduction of limestone.

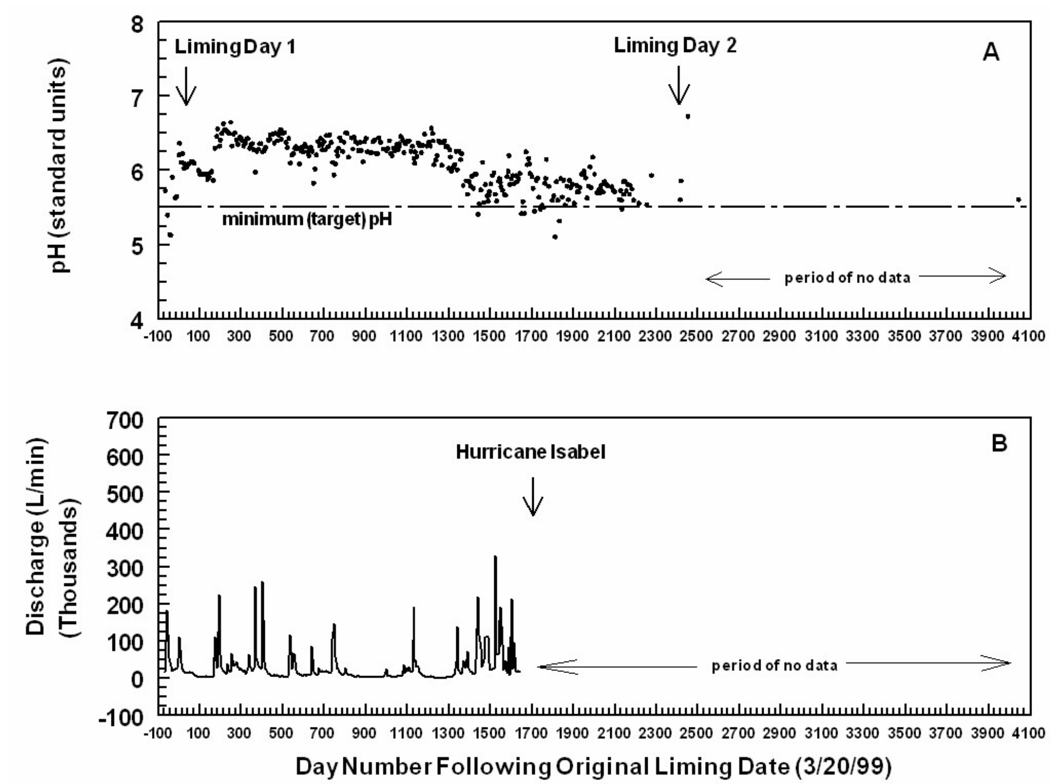

Figure 3: Values for pH (A) and discharge (B) for St. Mary's River SM 1. Discharge recording station was destroyed by Hurricane Isabel on Sept. 19, 2003 (Day 1644).

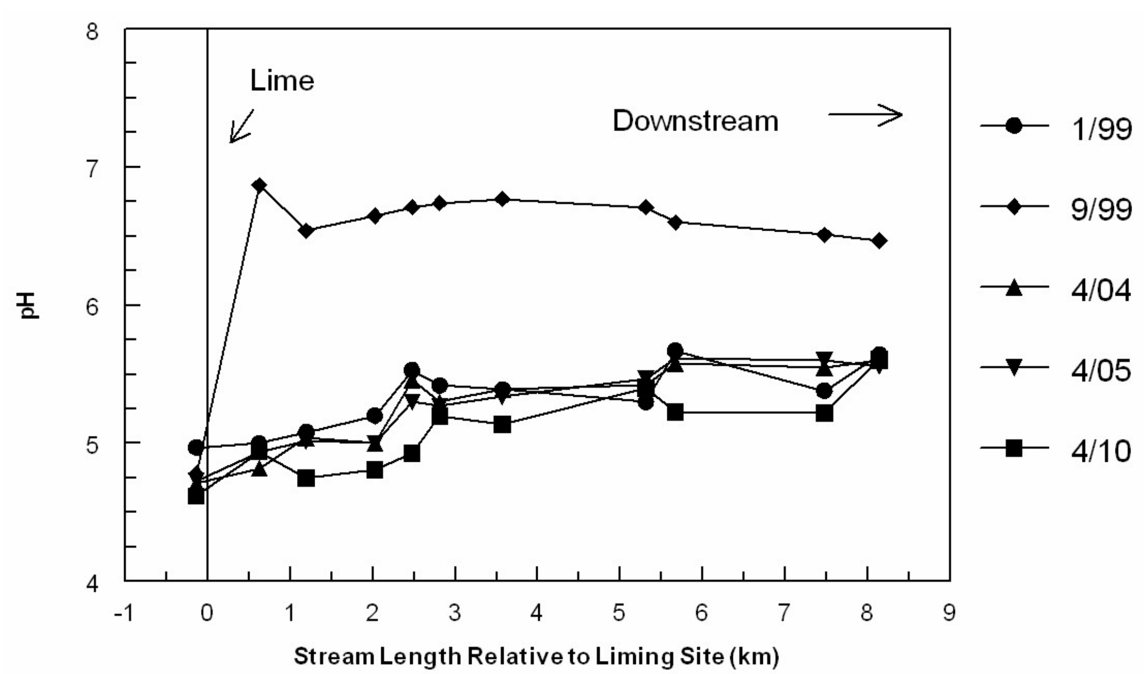

Figure 4: Values for pH measured for eleven sites (SM 1 – SM 11) at St. Mary's River. Selected quarterly results.

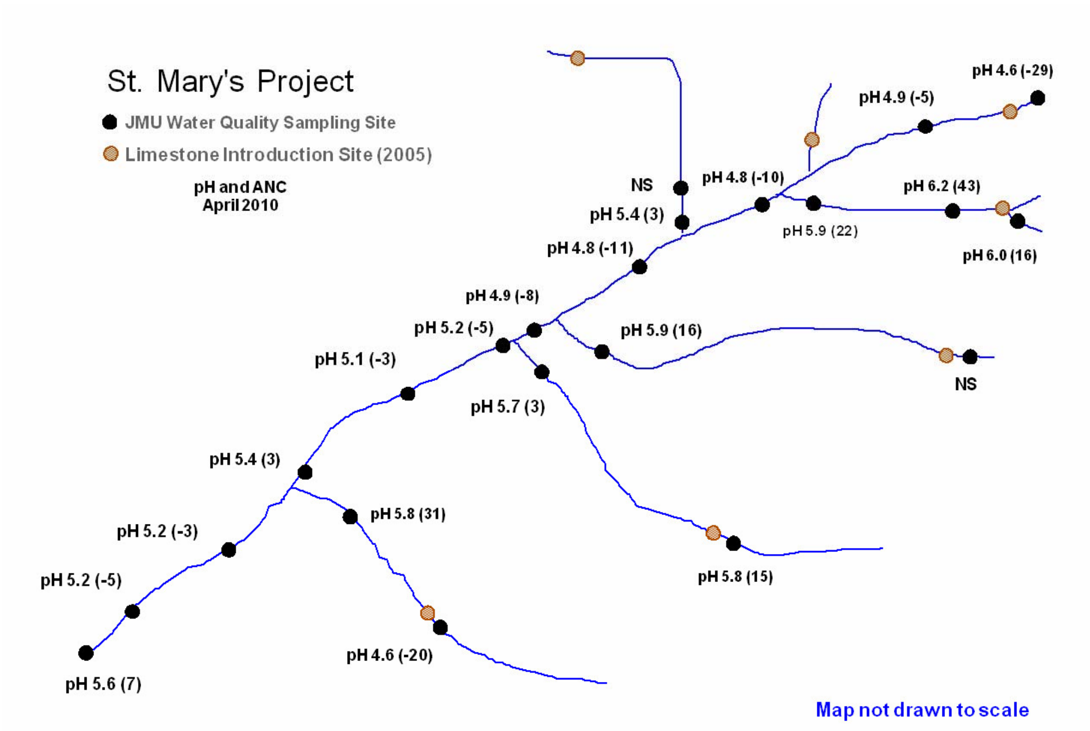

Figure 5: Map of St. Mary's Wilderness with the most recent (2010) pH and ANC values at sampled sites.

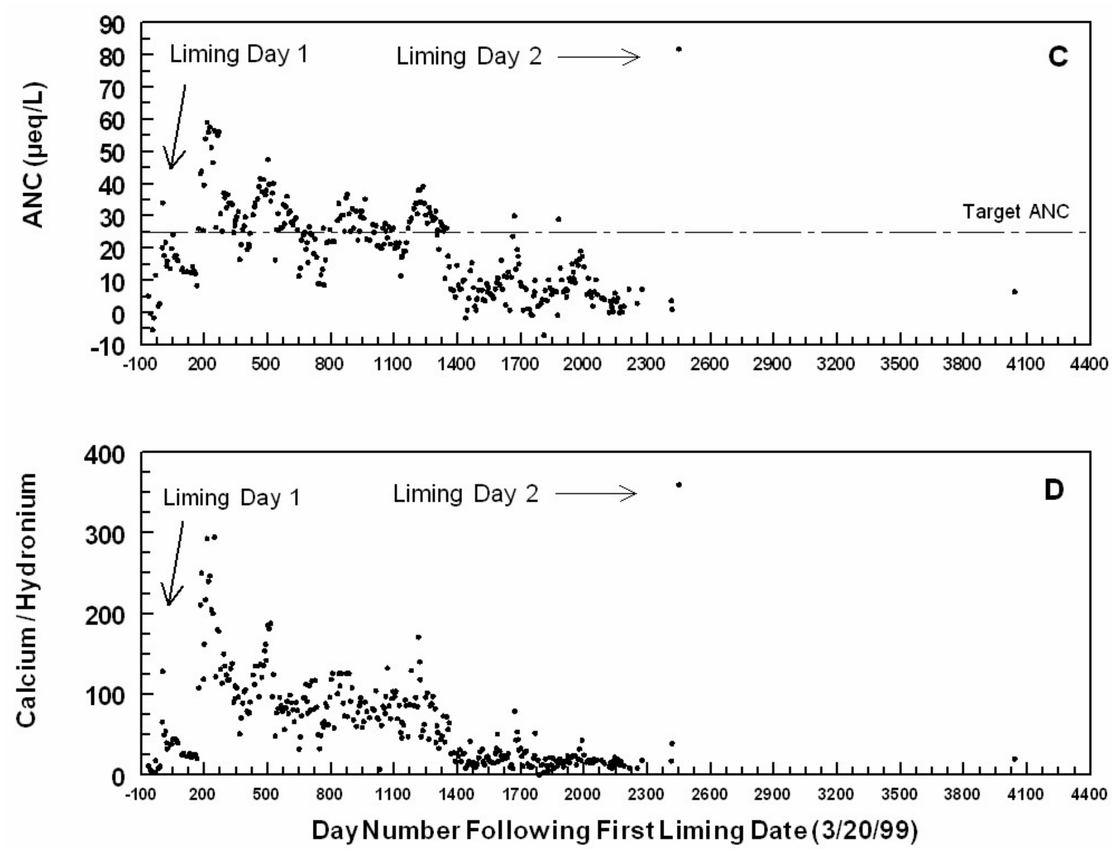

Figure 6: Values for ANC (C) and Calcium hydronium ratio (D) for St. Mary's River SM 1.

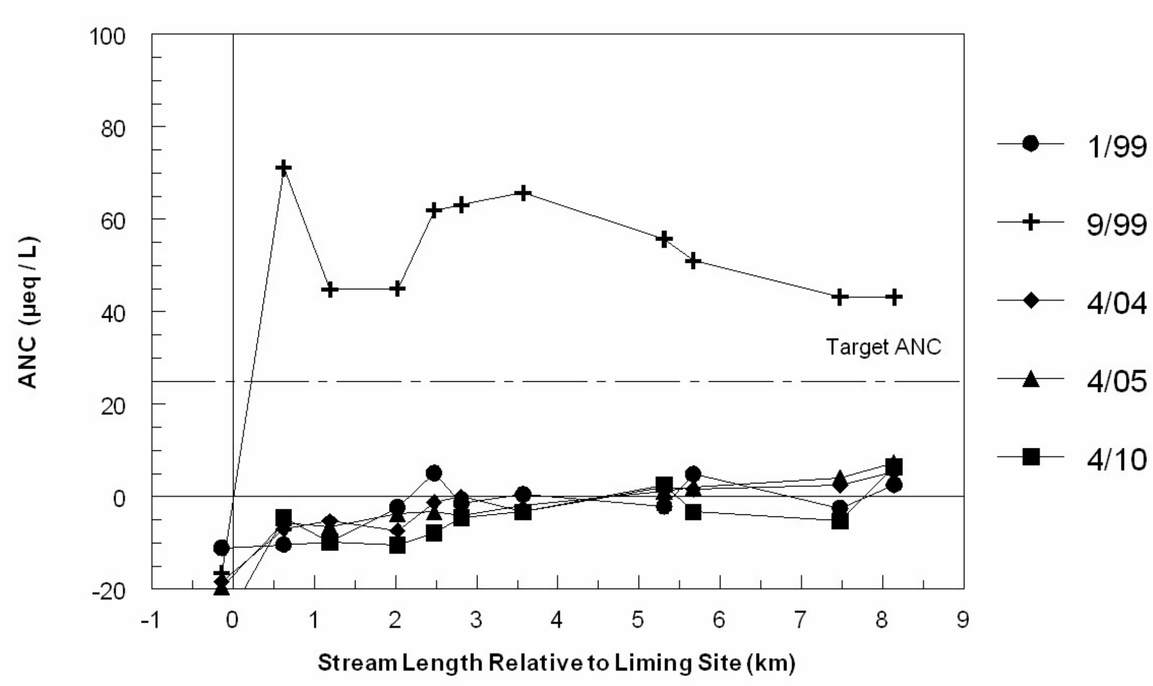

Figure 7: ANC values measured for eleven sites (SM 1 – SM 11) at St. Mary's River. Selected quarterly results.

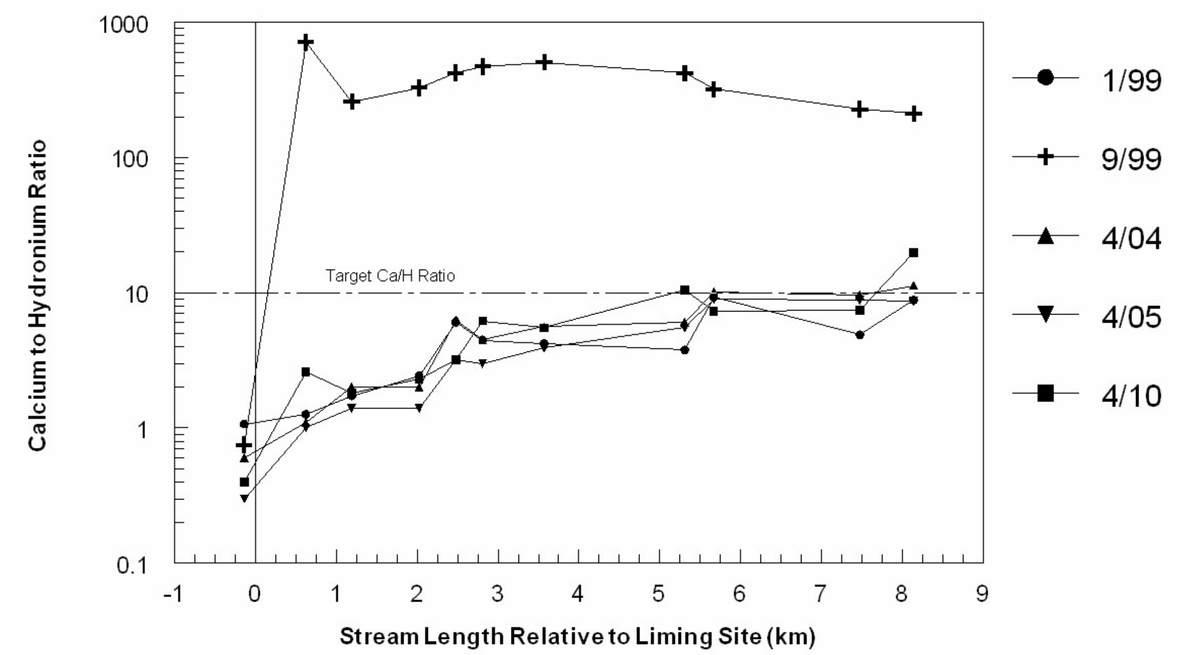

Figure 8: Calcium to hydronium ratio measured for eleven sites (SM 1 – SM 11) at St. Mary's River. Selected quarterly results.

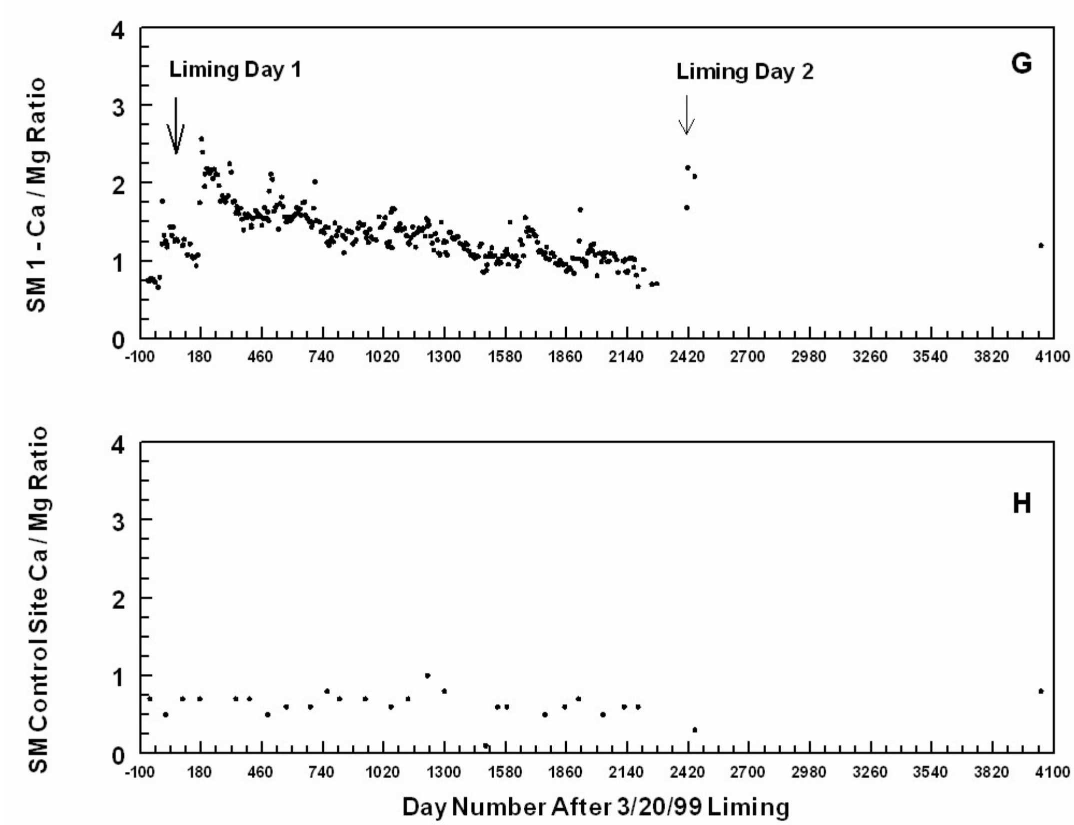

Figure 9: Calcium to magnesium ratio at a treated site (SM 1, G) and an untreated control site (SM 11, H). Weekly results shown for SM 1; quarterly results shown for SM 11.

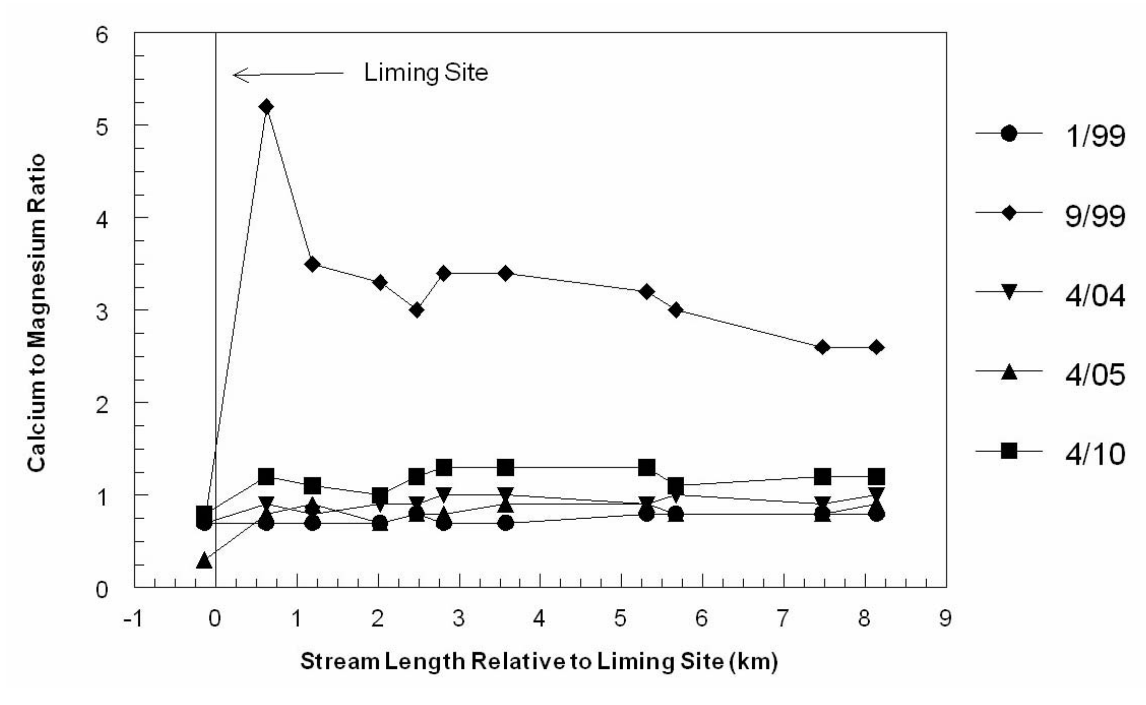

Figure 10: Calcium to magnesium ratio measured for eleven sites (SM 1 – SM 11) at St. Mary's River. Selected quarterly results.

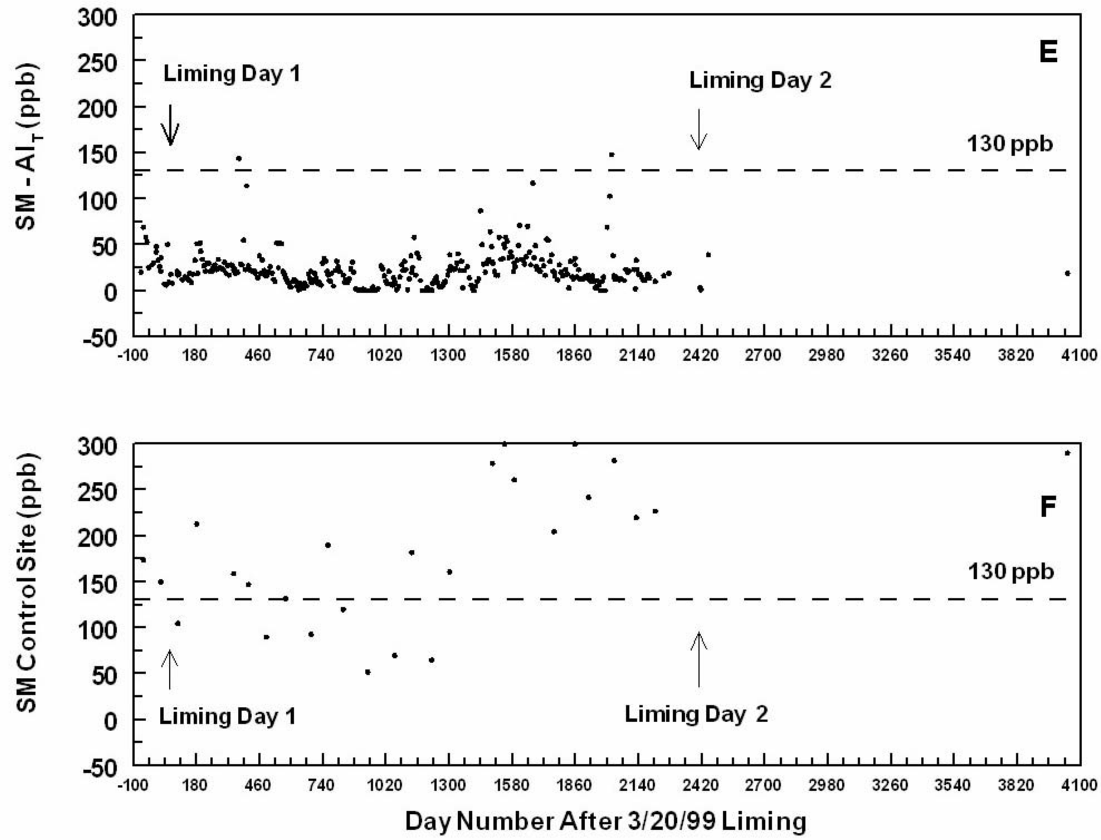

Figure 11: Aluminum concentration values (ppb) at a treated site (SM 1, E) and an untreated control site (SM 11, F). Weekly results shown for SM 1; quarterly results shown for SM 11.

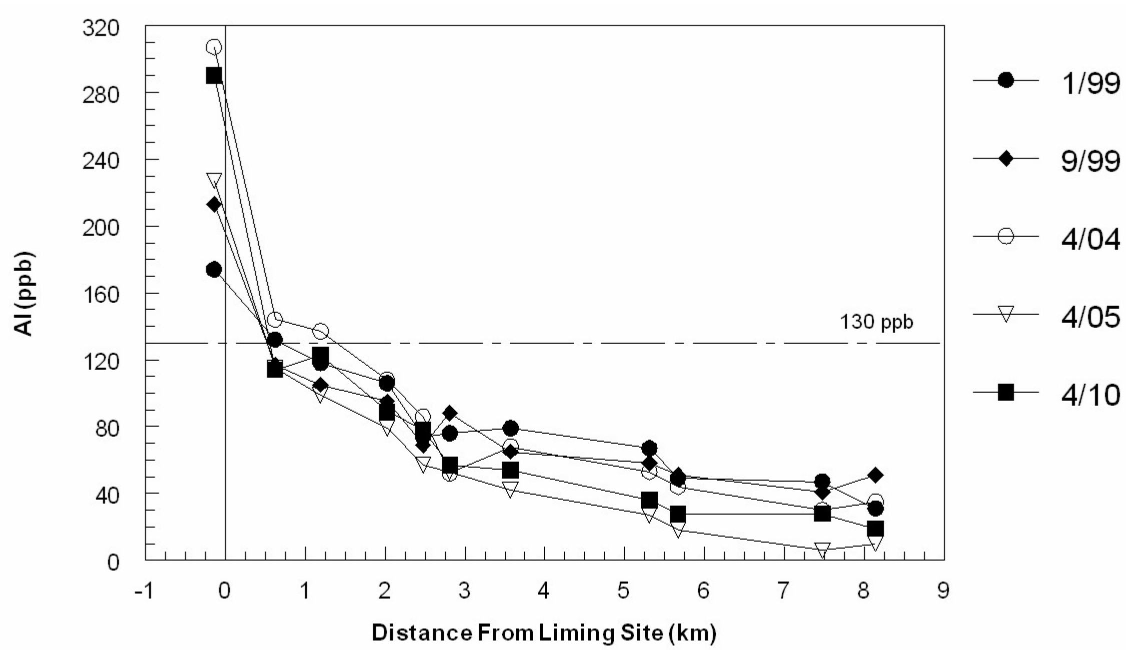

Figure 12: Aluminum concentration measured for eleven sites (SM 1 – SM 11) at St. Mary's River. Selected quarterly results.

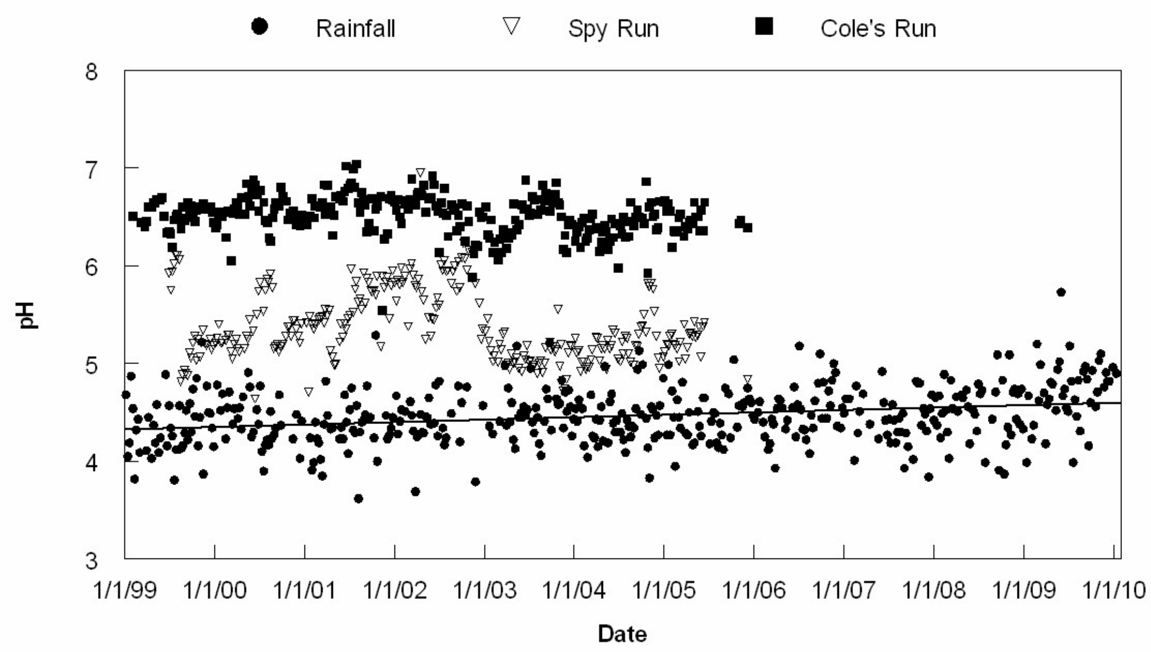

Figure 13: Weekly pH values of precipitation, Spy Run and Cole's Run. Precipitation values taken from data collected at Charlottesville Station, VA00 (National Acid Deposition Program, 2010). A fitted trend line is included for precipitation pH.

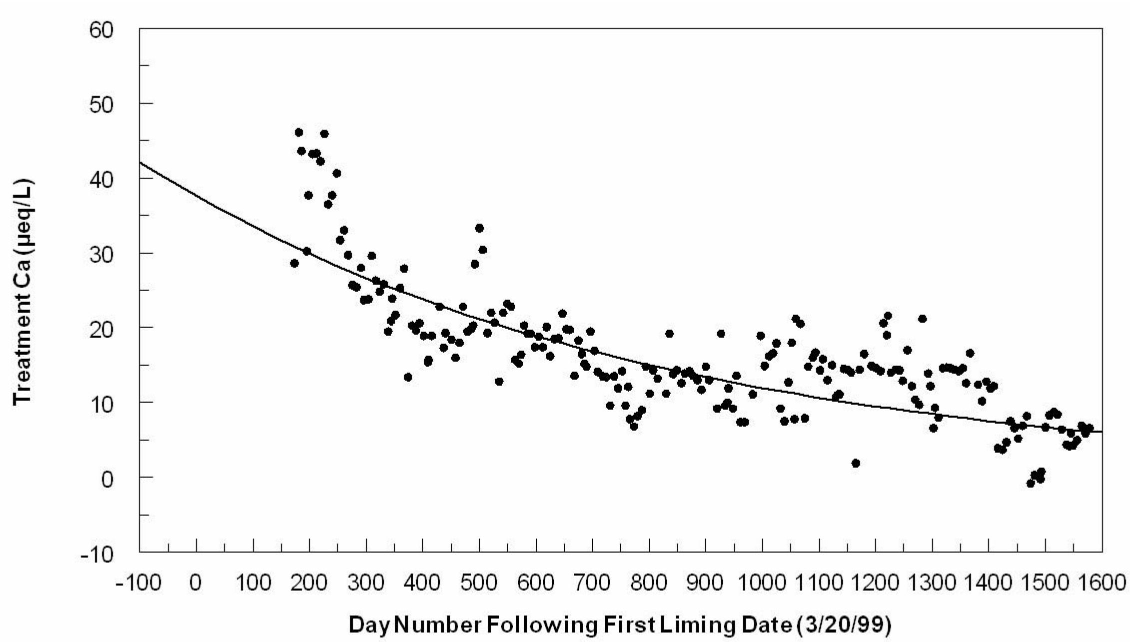

Figure 14: Calcium concentration by day number. Curve shows exponential decay for limestone consumption during the initial project period.

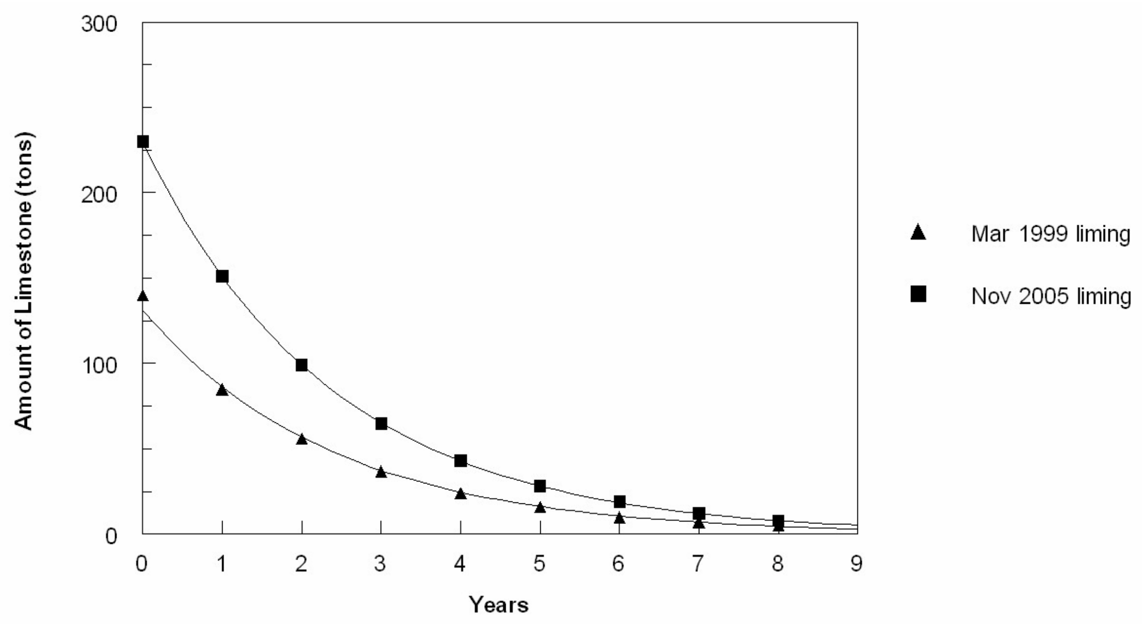

Figure 15: Idealized limestone consumption decay curves for treatments of 230 (■) and 140 (▲) tons with 1.65 year half-life.