

The Acid-Base Status of the St. Marys River: the Virginia Trout Stream Sensitivity Study Results

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INTRODUCTION

The St. Marys River in Augusta County is among the most well known and well studied of the upland streams in Virginia that have been affected by deposition of acidity from the atmosphere (Webb et al., 1989a; Cosby et al., 1991; Deviney & Webb, 1993). The Virginia Department of Game and Inland Fisheries has documented dramatic biological degradation in this stream consistent with acidification effects, including loss of both benthic and fish taxa (Kauffman et al., 1999; Bugas et al., 1999). The physiographic setting of the St. Marys watershed is similar to that of other streams in the Blue Ridge mountains where acidification related changes have been observed in stream water composition and aquatic biota (Ryan et al., 1989; Eshleman et al., 1995; Bulger et al., 1995).

Information concerning the acid-base status of surface waters in the St. Marys River watershed has been obtained through the Virginia Trout Stream Sensitivity Study (VTSSS). The VTSSS was designed to provide continuing information on the acid-base status of mountain headwater streams in western Virginia that support native brook trout (*Salvelinus fontinalis*). In the spring of 1987, a synoptic survey was conducted in which stream water samples were obtained for 344, or about 80%, of the region's identified native brook trout streams. Analysis of these samples indicated that a high proportion of this biologically defined population of streams is sensitive to acidification due to atmospheric deposition (Webb et al., 1989b). Following this survey, a sample (n = 65) of this stream population was selected for long-term monitoring and research. The selection criteria included relative absence of watershed disturbance, geographic representation, and coverage of the sensitivity range associated with the stream population. The St. Marys

River was among the most sensitive of the selected streams.

In this report, we provide a summary of water quality information collected for the St. Marys River watershed through the VTSSS program. We further provide an analysis of acid-base status in surface waters of the watershed. For this purpose, we focus on spatial and temporal variations in acid-neutralization capacity (ANC), a parameter which effectively indicates the balance between acids and bases in solution (Baker et al., 1990a). Surface water acidification, defined as a loss of ANC (Turner et al., 1990), occurs when concentrations of strong-acid anions (sulfate, nitrate, and chloride) increase relative to concentrations of base cations (calcium, magnesium, potassium, and sodium ions). If surface water ANC is reduced to sufficiently low values, acidity may increase, as indicated by a depression in pH, to a range associated with adverse effects on fish and other aquatic life (Baker & Christensen, 1991). Although surface water acidification involves a decrease in both ANC and pH, the relationship is nonlinear. At lower ANC levels, a given change in ANC results in more change in pH than occurs given the same change in ANC at higher ANC levels. The ANC of surface water is thus an indication of sensitivity to acidification, an indication of present acidity, and an indirect measure of surface water suitability for aquatic biota.

Watershed Description

The St. Marys River watershed is defined here as the approximately 26.9 km² drainage area above the VTSSS stream water sampling site designated VT41. This area is located on the western flank of the Blue Ridge Mountains in southeastern Augusta County and within the St. Marys Wilderness of the George Washington National Forest.

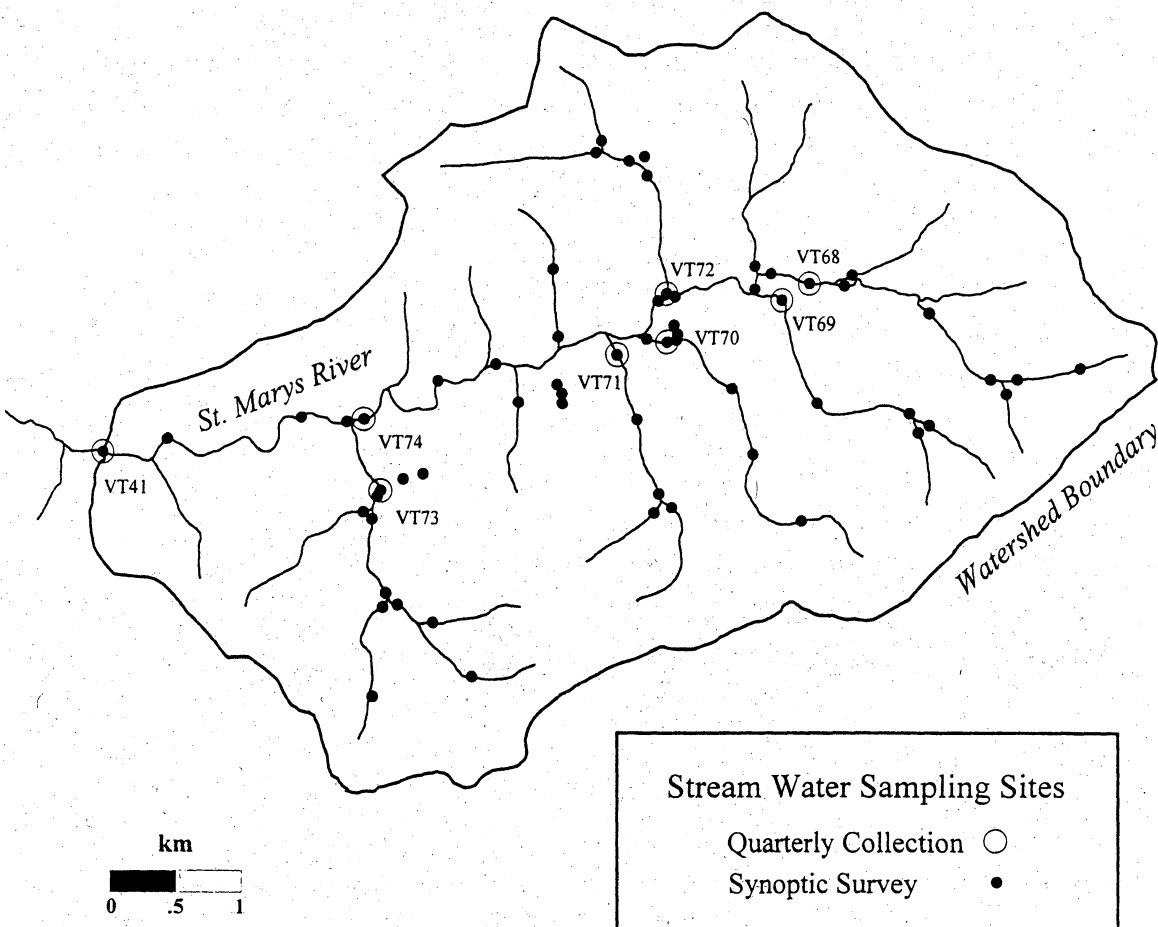


Fig. 1. VTSSS stream water sampling sites in the St. Marys River watershed.

VT41 is sited approximately 200 m upstream from the Wilderness boundary. Within the wilderness, the mainstem of the St. Marys River is approximately 9 km long, with six perennial tributaries. Approximately 3 km downstream from the wilderness boundary, the St. Marys River flows into the South River of the James River basin.

Watershed characteristics for the St. Marys River have been described by Deviney & Webb (1993). Terrain in the watershed is rocky and steep, except in some riparian areas along the mainstem. Elevations range from 530 to 1,100 m. Vegetative cover in the area is dominated by species with relatively low nutrient and moisture requirements such as chestnut oak (*Quercus prinus*), pitch pine (*Pinus rigida*), and mountain laurel (*Kalmia latifolia*). Large areas of the forest were defoliated by the larvae of the gypsy moth (*Lymantria dispar*) for several

successive years during the early 1990s. The geology of the watershed has been described by Werner (1966). Most of the watershed is underlain by the primarily siliciclastic rocks of the Chilhowee Group (Antietam, Hampton, and Unicoi Formations). Small portions are underlain by residual clay deposits of the Shady Formation and by basaltic rocks of the Catoctin Formation. Evidence of previous mining and processing of manganese ore, including pits and other disturbed areas, is present at several sites on or adjacent to exposures of the Shady Formation.

Since 1984, the St. Marys River watershed has been managed as a federally designated wilderness area. In response to evident losses of aquatic biota due to acidification, the USDA Forest Service has recently initiated a project to neutralize acidity in the St. Marys

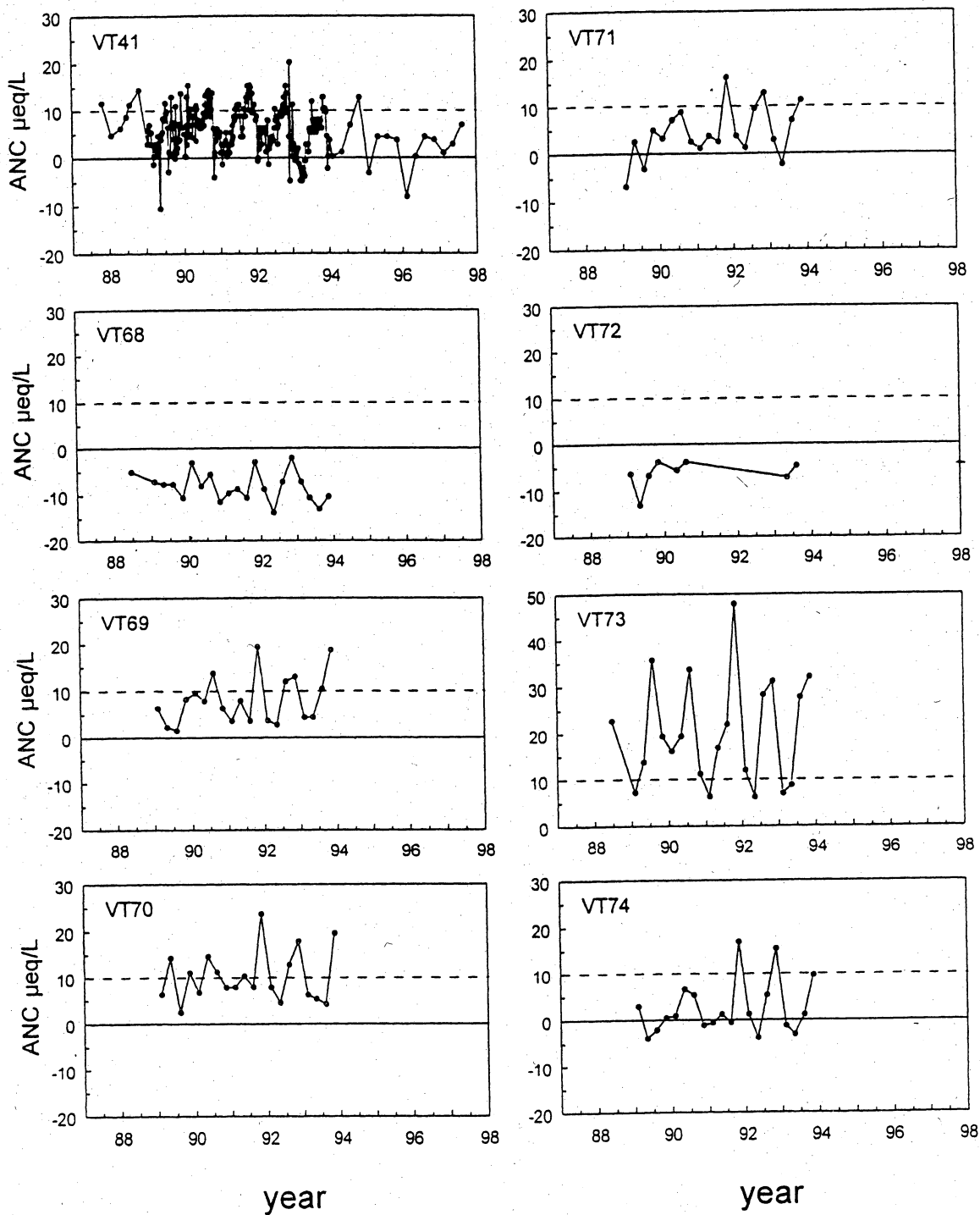


Fig. 2. ANC concentrations for VTSSS sampling sites in relation to ANC criteria for adverse biological effects associated with long term exposure (10 $\mu\text{eq/L}$) and short-term exposure (0 $\mu\text{eq/L}$).

River and the lower reaches of its major tributaries by direct application of limestone sand.

MATERIALS AND METHODS

Following the regional synoptic survey in the spring of 1987, seven sites on the mainstem and major tributaries of the St. Marys River were selected for quarterly sampling and analysis. Beginning in 1988, sampling frequency at VT41 was increased to weekly. Detailed synoptic sampling surveys were conducted in the watershed in March of 1992 (n = 62) and April of 1993 (n = 45). In 1993, sampling frequency at VT41 was reduced to quarterly and sampling at the other quarterly sites was

discontinued. A map of the St. Marys River watershed indicating sample locations is provided in Fig. 1. Geographic coordinates, elevations, and catchment areas of the quarterly sites are listed in Table 1.

Procedures for sample collection included use of prewashed polyethylene bottles, multiple rinses with stream water at the sample sites prior to sample collection, and maintenance of samples in insulated containers with refrigerant during transport to the project laboratory at the University of Virginia in Charlottesville, Virginia. Analysis was conducted for major dissolved constituents by methods commonly used for acid-deposition studies (e.g., USEPA, 1987; Morrison, 1991). Instrumentation and methods specifics are indicated in Table 2. Quality

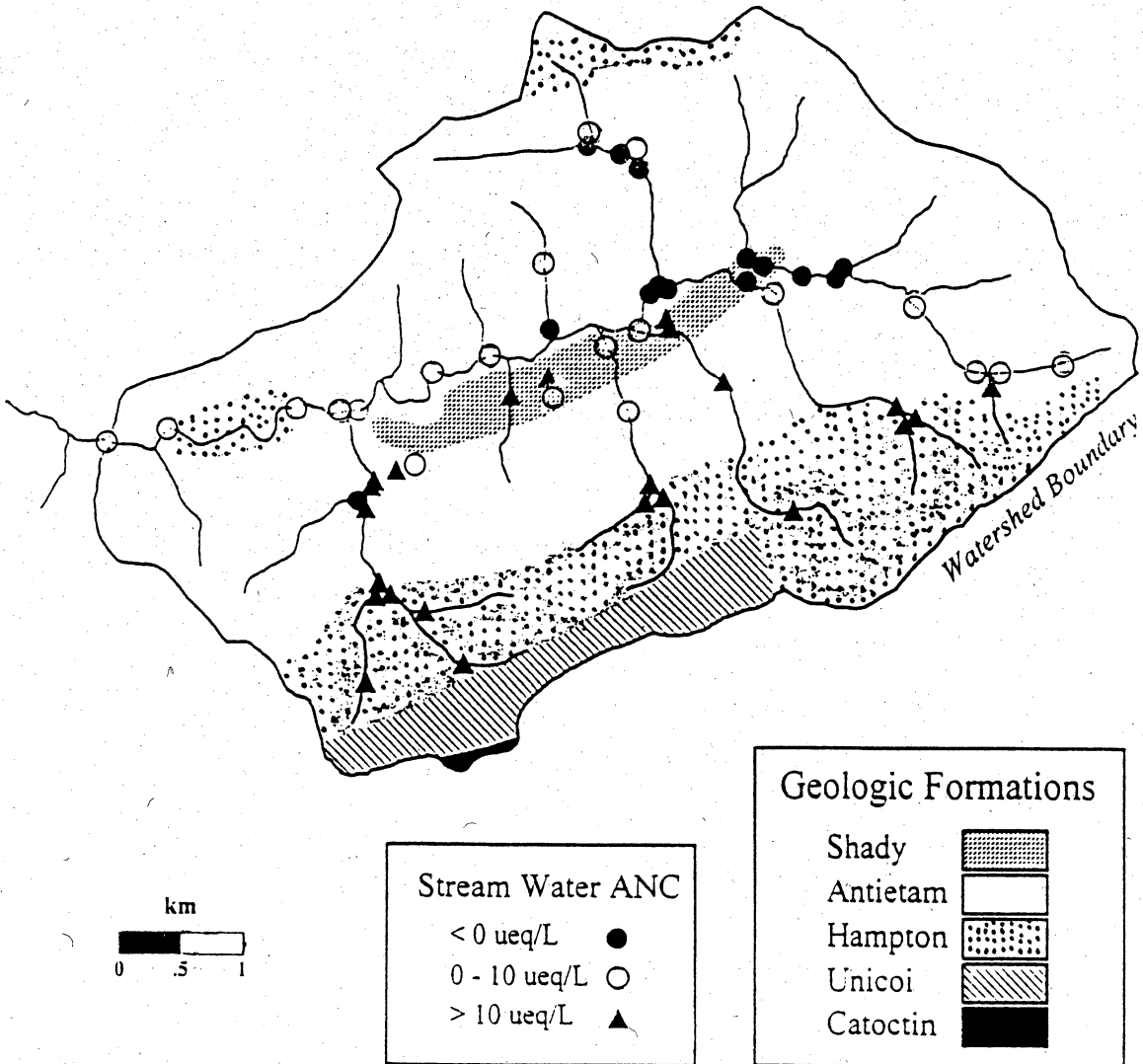


Fig. 3. ANC distribution for March 1992 synoptic stream sampling survey in St. Marys River watershed.

Table 1. VTSSS monitoring sites in the Saint Marys River watershed.

SITE	STREAM	MAPNAME	UTM-EW	UTM-NS	ELEV	AREA
VT41	ST MARYS -LOWER	VESUVIUS	663725	4198876	530	26.93
VT68	ST MARYS -UPPER	BIG LEVELS	669150	4200232	725	3.86
VT69	CHIMNEY BRANCH	BIG LEVELS	668936	4200105	725	1.99
VT70	BEAR BRANCH	BIG LEVELS	668052	4199789	677	2.14
VT71	MINE BANK CREEK	BIG LEVELS	667667	4199685	677	2.01
VT72	HOGBACK CREEK	BIG LEVELS	668039	4200139	689	2.17
VT73	SUGARTREE BRANCH	BIG LEVELS	665855	4198630	628	4.09
VT74	ST MARYS -MIDDLE	BIG LEVELS	665718	4199156	579	19.43

Notes: MAPNAME = USGS 7.5 Minute; ELEV = elevation in meters; AREA = catchment area in km²

Table 2. Laboratory Analytical Methods.

Aliquot	Instrumentation	Method
Acid-neutralization capacity	Bechman Psi pH Meter (No. 123114); Corning Calomel Combination pH Electrode (No. 476530)	Gran titration with 100 ml sample aliquot and 0.005 N HCl titrant. Within-aliquot stability (≤ 0.01 units/min.) obtained for endpoint determinations.
pH	Bechman Psi pH Meter (No. 123114); Corning Calomel Combination pH Electrode (No. 476530)	Potentiometric measurement with open-system samples. Within-aliquot stability (≤ 0.01 units/min.) and sequential aliquot agreement (≤ 0.03 units difference) obtained.
Calcium, Magnesium, Potassium, and Sodium	Thermo Jarrel Ash AA/AE Spectrophotometer Model Smith-Hieftje 22	Flame atomic absorption spectrophotometry. Li/La added to aliquot.
Sulfate, Nitrate, and Chloride	Dionex 4000I Ion Chromatograph; HPIC AS4A Separator Column; HPIC AG4A Pre-Column; AMMS Anion Micro-Membrane Suppressor	Simultaneous determination by ion chromatography. Injection volume: 200 μ L. Eluent: 2.2 mL 3.4-4.5 mM Na ₂ CO ₃ /minute. Regenerant: 3-4 ml 0.035 N H ₂ SO ₄ /minute.
Silica	Technicon Autoanalyzer II	Colorimetric detection by molybdate blue technique.
Aluminum, total monomeric	Technicon Autoanalyzer II	Colorimetric detection with open-system samples by pyrocatechol violet technique.

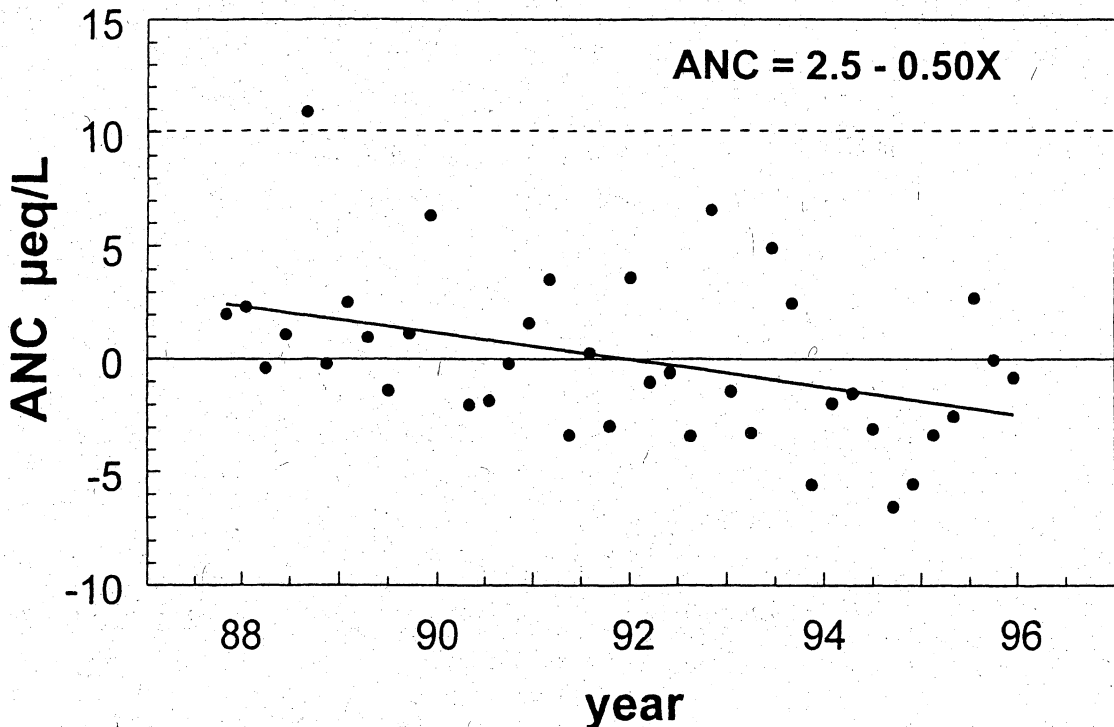


Fig. 4. Change in flow-adjusted ANC concentrations of St. Marys River (VT41) during the period of October 1987 to July 1997. The trend is significant at $P < 0.01$.

assurance procedures included determination of charge-balance error and analysis of sample duplicates, reference samples, and field blanks.

Although most VTSSS sites, including those in the St. Marys River watershed, are not gauged for discharge, we have used discharge data from USGS stations within 80 kilometers to interpolate daily discharge for VTSSS quarterly sample sites on days that samples were collected. For this purpose, discharge (cfs) for each USGS station was converted to runoff (mm/day) to normalize for unequal basin area.

RESULTS AND DISCUSSION

Table 3 lists the range and interquartile distributions of analyte concentration values for VTSSS stream water sampling sites in the St. Marys River watershed. ANC values for VTSSS monitoring sites in the St. Marys River watershed are plotted with time in Fig. 2.

The USDA Forest Service has devised ANC criteria for evaluation of potential acidification effects on aquatic

biota (Adams et al., 1991). An ANC value of 25 µeq/L was identified as the approximate lower limit of the range of ANC over which it is reasonably certain that fish and other aquatic organisms will not be affected by low pH and elevated aluminum concentrations. An ANC value of 10 µeq/L was identified as the value below which long-term exposure will likely cause adverse biological effects. An ANC value of 0 µeq/L was identified as the value below which short-term exposure will likely cause adverse biological effects. Consistent with observed losses of fish and macroinvertebrate taxa (Kauffman et al., 1999; Bugas et al., 1999), many of the ANC values for St. Marys River (Table 3 and Fig. 2) are below the indicated criteria for adverse effects on aquatic biota.

Fig. 2 also reveals the presence of both spatial and temporal variation in surface water ANC values in the watershed. In general, lower ANC values occur at sites in the upper part of the watershed and on tributaries draining from the north. These differences are consistent with associations between bedrock geology and stream water ANC observed in other areas of the Blue Ridge Moun-

tains (Lynch & Dise, 1985). Based on these associations, ANC values for stream waters draining the different bedrock formations in the watershed would be expected to decrease in the following order: Catoctin > Unicoi > Hampton > Antietam. This pattern is clearly evident in the distribution of stream water ANC values observed for the synoptic surveys. In Fig. 3, the ANC values for the March 1992 survey sites are displayed in relation to the mapped geologic formations. In general, the spatial variation of ANC in the watershed can be explained as a function of base-cation availability in the different rocks and associated soils. However, another factor may contribute to the relatively high ANC values in stream water draining the Shady Formation. Sulfate concentrations in these streams range from 5-15 $\mu\text{eq/L}$. This range is in the low end of the distribution observed for the synoptic surveys and much lower than the values observed for the quarterly monitoring sites (see Table 3). We suggest that the residual clay minerals associated with this formation may have an exceptionally high capacity for retention of atmospherically deposited sulfate. If so, this could affect ANC by altering the balance between concentrations of acid-anions and base-cations.

Several components of temporal variation are also apparent in Fig. 3. As commonly observed for upland surface waters (Baker et al., 1990b), cold season ANC values are generally lower than warm season values. Superimposed on this seasonal pattern is short-term variation determined by variation in discharge. This component is most apparent in the weekly data collected at VT41. Although discharge measurements are not available to allow direct examination of the flow-concentration relationship at this site, investigations in similar areas of the Blue Ridge Mountains (e.g., Eshleman et al., 1995) have shown that the lowest stream water ANC values occur on an episodic basis in association with high-discharge conditions.

Seasonal and episodic variation in the ANC of St. Marys River occur in a context of long-term or chronic change in ANC. In order to evaluate this change we performed trend analysis on the 10 years of quarterly data available for VT41. This analysis was performed in two steps using simple linear regression (SAS, 1991). Step one involved removal of background variation or "noise" related to discharge. As a preliminary step, we confirmed that there was no trend in estimated runoff during the 10-year period. Regression analysis was then applied to test the association between ANC and the estimated runoff values. This test was significant at $P < 0.001$. Step two was performed by application of regression analysis to test the association between time and the residuals of step one (interpreted as variation in ANC over and above that due

to variation caused by changes in runoff). This test was significant at $P < 0.01$, with an estimated slope of $-0.50 \mu\text{eq/L/yr}$ (Fig. 4). Additional tests were performed on the remaining residuals to confirm normality and constant error variance.

Based on the described trend analysis, the ANC of St. Marys River at site VT41 declined 5 $\mu\text{eq/L}$ during the period of 1988-1997. This change is substantial in relation to both the median ANC value of 4.4 $\mu\text{eq/L}$ for the 10-year period (Table 3) and the above cited USDA Forest Service criterion value of 0 $\mu\text{eq/L}$ for adverse biological effects given short-term exposure. It is also consistent with expectations of further acidification of central Appalachian streams due to elevated levels of atmospheric sulfur deposition. Cosby et al. (1991), Church et al. (1992), and Herlihy et al. (1993) have predicted that streams in this region will lose ANC as sulfur retention in watershed soils decreases over time. However, attribution of specific cause for the observed ANC change during this particular 10-year period will require additional analysis. Interpretation is complicated by dramatic alteration of stream water composition related to forest defoliation by the gypsy moth. Webb et al. (1995) and Eshleman et al. (1998) have documented changes in concentrations of nitrate, sulfate, base cations, and hydrogen ion that persisted for several years or more following defoliation. Until additional progress is achieved in modeling these effects, it will be difficult to partition the contributions of acidic deposition and forest defoliation to recent ANC change in the St. Marys River.

CONCLUSIONS

Stream water ANC in most of the St. Marys River watershed is below recognized criteria values for probability of adverse effects on aquatic fauna. Spatial variation in stream water ANC within the watershed is explained largely by the distribution of different bedrock types. Although it is clear that St. Marys River has experienced biologically significant acidification during the period of 1988-1997, the relative roles of acidic deposition and forest defoliation as causes for this acidification have not been determined.

ACKNOWLEDGEMENTS

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Table 3. Summary statistics (range and interquartile distribution) for analyses of stream water composition in the St. Marys River watershed.

ID	TYPE	START	STOP	N	MIN	25%	MED	75%	MAX
ANC ($\mu\text{eq/L}$)									
VT41	QUARTERLY	10/26/87	7/28/97	40	-8.1	1.2	4.4	6.9	15.4
VT41	WEEKLY	6/21/88	12/27/93	252	-27.9	2.8	6.2	8.7	20.3
VT68	QUARTERLY	6/21/88	10/28/93	21	-13.8	-10.6	-8.4	-7.2	-2.1
VT69	QUARTERLY	1/30/89	10/28/93	20	1.5	3.6	6.3	10.4	19.4
VT70	QUARTERLY	1/30/89	10/28/93	20	2.4	6.2	7.9	12.8	23.7
VT71	QUARTERLY	1/30/89	10/28/93	20	-6.8	1.2	3.2	7.0	16.2
VT72	QUARTERLY	1/30/89	7/28/93	8	-13.0	-7.2	-6.4	-4.7	-3.8
VT73	QUARTERLY	6/21/88	10/28/93	21	6.2	9.9	18.1	28.1	47.9
VT74	QUARTERLY	1/30/89	10/28/93	20	-3.9	-1.3	0.9	5.3	16.9
SYN1	SYNOPTIC	3/28/92	3/28/92	61	-19.7	-0.2	5.3	13.3	47.5
SYN2	SYNOPTIC	4/24/93	4/24/93	45	-25.0	-7.2	2.4	10.3	25.3
pH									
VT41	QUARTERLY	10/26/87	7/28/97	40	5.1	5.5	5.7	5.8	6.1
VT41	WEEKLY	6/21/88	12/27/93	252	5.1	5.6	5.8	5.9	6.8
VT68	QUARTERLY	6/21/88	10/28/93	21	4.9	5.0	5.1	5.1	5.3
VT69	QUARTERLY	1/30/89	10/28/93	20	5.3	5.7	5.8	5.9	6.0
VT70	QUARTERLY	1/30/89	10/28/93	20	5.2	5.8	5.9	5.9	6.1
VT71	QUARTERLY	1/30/89	10/28/93	20	5.5	5.6	5.7	5.8	6.0
VT72	QUARTERLY	1/30/89	7/28/93	8	5.0	5.0	5.1	5.3	5.3
VT73	QUARTERLY	6/21/88	10/28/93	21	5.3	5.9	6.0	6.2	6.4
VT74	QUARTERLY	1/30/89	10/28/93	20	5.2	5.5	5.6	5.8	6.2
SYN1	SYNOPTIC	3/28/92	3/28/92	61	4.7	5.3	5.8	6.1	6.6
SYN2	SYNOPTIC	4/24/93	4/24/93	45	4.6	5.1	5.6	6.1	6.4
Calcium ($\mu\text{eq/L}$)									
VT41	QUARTERLY	10/26/87	7/28/97	40	20.4	22.0	22.8	24.4	27.6
VT41	WEEKLY	6/21/88	12/27/93	252	17.8	22.1	23.7	25.0	45.5
VT68	QUARTERLY	6/21/88	10/28/93	21	9.7	12.2	13.0	13.5	15.7
VT69	QUARTERLY	1/30/89	10/28/93	20	16.0	17.2	18.0	18.8	20.3
VT70	QUARTERLY	1/30/89	10/28/93	20	17.1	18.7	20.0	20.7	22.5
VT71	QUARTERLY	1/30/89	10/28/93	20	15.0	16.2	17.2	18.0	19.6
VT72	QUARTERLY	1/30/89	7/28/93	8	12.5	14.0	17.4	19.0	21.6
VT73	QUARTERLY	6/21/88	10/28/93	21	23.2	30.6	32.2	37.3	42.3
VT74	QUARTERLY	1/30/89	10/28/93	20	16.7	19.3	20.9	21.8	23.6
SYN1	SYNOPTIC	3/28/92	3/28/92	61	4.6	14.4	18.4	24.5	45.9
SYN2	SYNOPTIC	4/24/93	4/24/93	45	9.4	14.5	16.8	24.0	43.5

Table 3. Continued.

ID	TYPE	START	STOP	N	MIN	25%	MED	75%	MAX
Magnesium ($\mu\text{eq/L}$)									
VT41	QUARTERLY	10/26/87	7/28/97	40	25.7	27.1	28.1	30.3	33.7
VT41	WEEKLY	6/21/88	12/27/93	252	23.4	27.2	29.3	30.9	57.0
VT68	QUARTERLY	6/21/88	10/28/93	21	15.5	18.0	18.8	19.5	20.4
VT69	QUARTERLY	1/30/89	10/28/93	20	21.6	22.8	24.4	25.0	26.0
VT70	QUARTERLY	1/30/89	10/28/93	20	20.1	21.8	22.9	23.6	24.8
VT71	QUARTERLY	1/30/89	10/28/93	20	21.0	22.6	23.8	24.3	26.3
VT72	QUARTERLY	1/30/89	7/28/93	8	17.8	18.6	21.7	23.7	26.6
VT73	QUARTERLY	6/21/88	10/28/93	21	28.6	37.3	39.4	41.8	52.1
VT74	QUARTERLY	1/30/89	10/28/93	20	21.8	24.3	25.6	26.8	28.4
SYN1	SYNOPTIC	3/28/92	3/28/92	61	9.9	20.4	24.2	29.8	44.4
SYN2	SYNOPTIC	4/24/93	4/24/93	45	14.8	20.8	23.9	29.7	40.4

Sodium ($\mu\text{eq/L}$)

VT41	QUARTERLY	10/26/87	7/28/97	40	15.5	16.9	17.4	17.8	20.5
VT41	WEEKLY	6/21/88	12/27/93	252	13.0	16.8	17.4	18.0	24.3
VT68	QUARTERLY	6/21/88	10/28/93	21	13.8	14.5	15.4	15.9	19.0
VT69	QUARTERLY	1/30/89	10/28/93	20	16.6	17.2	17.9	18.6	19.2
VT70	QUARTERLY	1/30/89	10/28/93	20	15.3	16.0	16.9	17.3	17.9
VT71	QUARTERLY	1/30/89	10/28/93	20	15.2	15.8	16.9	17.7	18.4
VT72	QUARTERLY	1/30/89	7/28/93	8	13.7	14.4	15.2	16.1	17.1
VT73	QUARTERLY	6/21/88	10/28/93	21	19.7	20.9	22.1	23.1	25.2
VT74	QUARTERLY	1/30/89	10/28/93	20	14.4	15.0	15.5	16.3	17.3
SYN1	SYNOPTIC	3/28/92	3/28/92	61	12.1	14.8	16.1	17.7	24.4
SYN2	SYNOPTIC	4/24/93	4/24/93	45	12.1	14.5	15.9	17.1	23.8

Potassium ($\mu\text{eq/L}$)

VT41	QUARTERLY	10/26/87	7/28/97	40	14.2	16.3	17.2	18.3	20.4
VT41	WEEKLY	6/21/88	12/27/93	252	11.8	16.4	17.4	18.6	32.9
VT68	QUARTERLY	6/21/88	10/28/93	21	8.2	11.2	12.0	12.9	14.2
VT69	QUARTERLY	1/30/89	10/28/93	20	18.7	22.6	23.5	25.1	26.6
VT70	QUARTERLY	1/30/89	10/28/93	20	15.0	18.1	19.3	20.8	22.9
VT71	QUARTERLY	1/30/89	10/28/93	20	16.7	18.8	20.4	22.9	25.4
VT72	QUARTERLY	1/30/89	7/28/93	8	12.8	17.9	18.8	20.3	21.2
VT73	QUARTERLY	6/21/88	10/28/93	21	21.1	24.3	25.2	27.2	31.8
VT74	QUARTERLY	1/30/89	10/28/93	20	12.1	14.4	15.1	16.4	20.3
SYN1	SYNOPTIC	3/28/92	3/28/92	61	4.0	13.7	16.7	22.1	28.8
SYN2	SYNOPTIC	4/24/93	4/24/93	45	5.3	14.9	17.6	24.2	30.8

Sulfate ($\mu\text{eq/L}$)

VT41	QUARTERLY	10/26/87	7/28/97	40	50.1	53.8	61.9	65.3	74.1
VT41	WEEKLY	6/21/88	12/27/93	252	46.5	53.5	60.9	65.1	114.1
VT68	QUARTERLY	6/21/88	10/28/93	21	46.5	49.9	54.6	56.4	62.7
VT69	QUARTERLY	1/30/89	10/28/93	20	45.1	48.6	54.4	56.5	59.6
VT70	QUARTERLY	1/30/89	10/28/93	20	36.8	39.1	45.2	47.8	52.6
VT71	QUARTERLY	1/30/89	10/28/93	20	44.6	47.8	52.1	54.2	57.2
VT72	QUARTERLY	1/30/89	7/28/93	8	48.0	49.2	60.4	66.3	75.4
VT73	QUARTERLY	6/21/88	10/28/93	21	65.2	70.2	74.3	76.5	91.3
VT74	QUARTERLY	1/30/89	10/28/93	20	42.9	46.0	57.4	60.5	66.9
SYN1	SYNOPTIC	3/28/92	3/28/92	61	5.0	44.9	55.1	60.8	84.2
SYN2	SYNOPTIC	4/24/93	4/24/93	45	28.1	47.5	61.4	65.5	92.9

Table 3. Continued.

ID	TYPE	START	STOP	N	MIN	25%	MED	75%	MAX
Nitrate ($\mu\text{eq/L}$)									
VT41	QUARTERLY	10/26/87	7/28/97	40	0.0	0.0	0.2	2.4	6.7
VT41	WEEKLY	6/21/88	12/27/93	252	0.0	0.2	0.3	2.8	16.5
VT68	QUARTERLY	6/21/88	10/28/93	21	0.0	0.1	0.2	0.2	1.2
VT69	QUARTERLY	1/30/89	10/28/93	20	0.0	0.1	0.2	2.0	7.9
VT70	QUARTERLY	1/30/89	10/28/93	20	0.0	0.1	0.2	3.3	7.9
VT71	QUARTERLY	1/30/89	10/28/93	20	0.0	0.1	0.2	1.1	5.9
VT72	QUARTERLY	1/30/89	7/28/93	8	0.1	0.1	0.2	0.2	1.1
VT73	QUARTERLY	6/21/88	10/28/93	21	0.0	0.1	0.4	7.2	15.0
VT74	QUARTERLY	1/30/89	10/28/93	20	0.0	0.1	0.2	0.9	4.1
SYN1	SYNOPTIC	3/28/92	3/28/92	61	0.1	0.4	1.5	4.1	22.3
SYN2	SYNOPTIC	4/24/93	4/24/93	45	0.3	1.1	1.9	8.0	25.5

Chloride ($\mu\text{eq/L}$)

VT41	QUARTERLY	10/26/87	7/28/97	40	14.7	15.7	16.3	17.5	21.3
VT41	WEEKLY	6/21/88	12/27/93	252	11.5	15.5	16.2	16.8	34.3
VT68	QUARTERLY	6/21/88	10/28/93	21	13.9	14.3	15.4	15.8	16.8
VT69	QUARTERLY	1/30/89	10/28/93	20	13.3	14.3	15.2	15.7	17.2
VT70	QUARTERLY	1/30/89	10/28/93	20	13.5	14.3	15.1	15.6	16.5
VT71	QUARTERLY	1/30/89	10/28/93	20	13.5	13.9	14.7	15.3	16.9
VT72	QUARTERLY	1/30/89	7/28/93	8	14.1	14.2	14.9	15.6	15.7
VT73	QUARTERLY	6/21/88	10/28/93	21	15.3	16.3	17.3	18.3	19.5
VT74	QUARTERLY	1/30/89	10/28/93	20	14.1	14.7	15.4	15.7	16.4
SYN1	SYNOPTIC	3/28/92	3/28/92	61	12.8	14.5	15.0	16.2	21.8
SYN2	SYNOPTIC	4/24/93	4/24/93	45	12.2	14.1	14.9	16.4	19.8

Silica ($\mu\text{m/L}$)

VT41	QUARTERLY	10/26/87	7/28/97	40	62.4	67.4	71.9	85.2	94.5
VT41	WEEKLY	6/21/88	12/27/93	252	54.0	69.0	74.7	83.7	101.4
VT68	QUARTERLY	6/21/88	10/28/93	21	53.6	58.0	62.7	70.4	76.1
VT69	QUARTERLY	1/30/89	10/28/93	20	64.8	68.2	69.8	76.9	91.8
VT70	QUARTERLY	1/30/89	10/28/93	20	62.7	65.1	67.5	77.5	90.0
VT71	QUARTERLY	1/30/89	10/28/93	20	60.8	63.4	67.6	77.7	87.3
VT72	QUARTERLY	1/30/89	7/28/93	8	59.6	65.0	69.9	79.0	89.0
VT73	QUARTERLY	6/21/88	10/28/93	21	74.8	78.8	81.8	91.9	97.1
VT74	QUARTERLY	1/30/89	10/28/93	20	58.4	65.0	68.3	82.8	97.0
SYN1	SYNOPTIC	3/28/92	3/28/92	61	49.4	59.6	63.0	67.2	87.5
SYN2	SYNOPTIC	4/24/93	4/24/93	45	43.8	58.3	61.4	64.9	81.2

Total Monomeric Aluminum ($\mu\text{g/L}$)

VT41	QUARTERLY	1/26/94	4/28/97	14	11.6	13.8	19.3	31.9	66.0
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LITERATURE CITED

- Adams, M.B., D.S. Nichols, C.A. Federer, K.F. Jensen, & H. Parrott. 1991. Screening Procedure to Evaluate Effects of Air Pollution on Eastern Region Wildernesses Cited as Class I Air Quality Areas. General Technical Report NE-151, USDA-Forest Service, Northeastern Forest Experiment Station, Radnor, PA.
- Baker, L.A., P.R. Kaufmann, A.T. Herlihy, & J.M. Eiler. 1990a. Current status of surface water acid-base chemistry. Pp. 9-5 - 9-336 *In* P.M. Irving (ed.), *Acidic Deposition: State of Science and Technology*. National Acid Precipitation Assessment Program, Washington, D.C.
- Baker, J.P., D.P. Bernard, S.W. Christensen, & M.J. Sale. 1990b. Biological effects of changes in surface water acid-base chemistry. Pp. 13-1 - 13-381 *In* P.M. Irving (ed.), *Acidic Deposition: State of Science and Technology*. National Acid Precipitation Assessment Program, Washington, D.C.
- Baker, J.P., & S.W. Christensen. 1991. Effects of acidification on biological communities in aquatic ecosystems. Pp. 83-106 *In* D.F. Charles (ed.), *Acid Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, NY.
- Bugas, Jr., P.E., L.O. Mohn, & J.W. Kauffman. 1999. Impacts of acid deposition on fish populations in the St. Marys River, Augusta County, Virginia. *Banisteria* 13:191-200.
- Bulger, A.J., C.A. Dolloff, B. J. Cosby, K.N. Eshleman, J.R. Webb, & J.N. Galloway. 1989. The "Shenandoah National Park: Fish in Sensitive Habitats (SNP: FISH)" project: an integrated assessment of fish community responses to stream acidification. *Water, Air, and Soil Pollution* 85: 309-314.
- Church M.R., P.W. Shaffer, D.L. Thornton, D.L. Cassell, C.I. Liff, M.G. Johnson, D.A. Lammers, J.J. Lee, G.R. Holdren, J.S. Kern, L.H. Liegel, S.M. Pierson, D.L. Stevens, & B.P. Rochelle. 1992. Direct/Delayed Response Project: Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Mid-Appalachian Region of the Eastern United States. Report 600/R-92/186. USEPA, Washington, DC.
- Cosby, B.J., P.F. Ryan, J.R. Webb, G.M. Hornberger, & J.N. Galloway. 1991. Mountains of western Virginia. Pp. 297-318 *In* D.F. Charles (ed.), *Acid Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, NY.
- Deviney, Jr., F.A., & J.R. Webb. 1993. St. Mary's River Watershed Database Reference. Report to USDA Forest Service, Roanoke, VA. 86 pp.
- Eshleman, K.N., L.M. Miller-Marshall, & J.R. Webb. 1995. Long-term changes in episodic acidification of streams in Shenandoah National Park, Virginia (USA). *Water, Air, and Soil Pollution* 85: 517-522.
- Eshleman, K.N., R.P. Morgan II, J.R. Webb, F.A. Deviney, & J.N. Galloway. 1998. Temporal patterns of nitrogen leakage from mid-Appalachian forested watersheds: role of insect disturbances. *Water Resources Research* 34:2005-2116.
- Herlihy, A.T., P.R. Kaufmann, M.R. Church, P.J. Wigington, J.R. Webb, & M.J. Sale. 1993. The effects of acidic deposition on streams in the Appalachian mountain and Piedmont region of the mid-Atlantic United States. *Water Resources Research* 29: 2687-2703.
- Kauffman J.W., L.O. Mohn, & P.E. Bugas, Jr. 1999. Effects of acidification on benthic fauna in St. Marys River, Augusta County, Virginia. *Banisteria* 13:183-190.
- Lynch, D.D., & N.B. Dise. 1985. Sensitivity of stream basins in Shenandoah National Park to acid deposition. U.S. Geological Survey, Water-Resources Investigations Report, 85-4115. 61 pp.
- Morrison, M.L. 1991. Part 1: Quality Assurance Plan for the Long-Term Monitoring Project, in Data User's Guide to the U.S. EPA Long-Term Monitoring Project: Quality Assurance Plan and Data Dictionary. EPA/600/3-91-072. U.S. EPA Environmental Research Laboratory, Corvallis, OR.
- Ryan, P.F., G.M. Hornberger, B.J. Cosby, J.N. Galloway, J.R. Webb, & E.B. Rastetter. 1989. Changes in the chemical composition of stream water in two catchments in the Shenandoah National Park, VA, in response to atmospheric deposition of sulfur. *Water Resources Research* 25: 2091-2099.
- SAS. 1991. SAS/STAT User's Guide, Version 6, Vol.1. SAS Institute, Inc., Cary, NC. 1,686 pp.
- Turner, R.S., R.B. Cook, H. Van Miegroet, D.W. Johnson, J.W. Elwood, O.P. Bricker, S.E. Linderg, & G.M. Hornberger. 1990. Watershed and lake processes affecting

surface water acid-base chemistry. Pp. 10-1 - 10-167 *In* P.M. Irving (ed.), *Acidic Deposition: State of Science and Technology*. National Acid Precipitation Assessment Program, Washington, D.C.

U.S. Environmental Protection Agency (USEPA). 1987. *Handbook of Methods for Acid Deposition Studies: Laboratory Analysis for Surface Water Chemistry*, EPA/600/4-87/026, USEPA, Washington, D.C.

Webb, J.R., P.E. Bugas, B.J. Cosby, J.N. Galloway, G.M. Hornberger, J.W. Kauffman, L.O. Mohn, P.F. Ryan, & P.P. Smith. 1989a. Acidic deposition and the status of Virginia's wild trout resource. Pp. 228-233. F.

Richardson & R. H. Hamre (eds.), *In* Wild Trout IV, Proceedings of the Symposium, Yellowstone National

Park, Laramie, WY.

Webb, J.R., B.J. Cosby, J.N. Galloway, & G.M. Hornberger. 1989b. Acidification of native brook trout streams in Virginia. *Water Resources Research* 25:1367-1377.

Webb, J. R., B.J. Cosby, F.A. Deviney, K.N. Eshleman, & J.N. Galloway. 1995. Change in the acid-base status of an Appalachian Mountain catchment following forest defoliation by the gypsy moth. *Water, Air and Soil Pollution* 85:535-540.

Werner, H.J. 1966. *Geology of the Vesuvius Quadrangle*. Virginia Division of Mineral Resources, Charlottesville, VA 53 pp.