The Pennsylvania State University

The Graduate School

College of Agricultural Sciences

EFFECTS OF WATERSHED ACIDIFICATION ON SOIL CHEMISTRY, RADIAL GROWTH, AND BOLEWOOD CHEMISTRY OF THREE HARDWOOD SPECIES IN WEST VIRGINIA

A Thesis in

Environmental Pollution Control

by

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ABSTRACT

The effects of watershed acidification due to ammonium sulfate treatments on soil fertility, bolewood chemistry and radial growth were studied on the Fernow Experimental Forest near Parsons, WV. This research represented an evaluation of the impacts of 12 years of simulated acidification, using ammonium sulfate treatments, on the health and growth of yellow poplar (*Liriodendron tulipifera*), black cherry (*Prunus serotina*), and red maple (*Acer rubrum*) trees. The objectives of this study were: 1) to determine the effects of long-term artificial watershed acidification on the dendrochemistry or bolewood of black cherry, yellow poplar, and red maple trees, 2) to determine the impacts of artificial long-term acidification on radial and basal area growth rates of all three tree species. Tree cores and soil samples were taken from an acidified (WS3) and a control (WS7) watershed during late summer of 2000 for chemical analysis. A growth analysis was completed on each tree species to detect any growth differences between trees on the control and treated watersheds. Analysis of soil samples revealed that 12 years of acidification caused significant base cation depletion and decreased calcium-aluminum (Ca/Al) molar ratios relative to both the control and historical data on the same watersheds. Wood chemistry results indicated that on the acidified watershed, black cherry and yellow poplar had significantly lower Ca concentrations, significantly higher manganese (Mn) concentrations, and significantly lower Ca/Mn and magnesium (Mg)/Mn molar ratios in the wood formed during 1997 to 2000 than previous years, indicating a mobilization-depletion effect for base cations in the wood of these two species. Red maple wood chemistry was not significantly different between control and treated watersheds. Radial growth rates for black cherry and yellow poplar supported the mobilization-depletion effect on the treated watershed. Radial growth initially increased and subsequently decreased in concert with the apparent mobilization and then depletion of base cations. Radial growth of treated red maple trees was also less than control trees, but the difference was not significant. Basal area increment calculations from growth data indicated that all three tree species on the treated watershed were growing slower than control trees eight to twelve years after treatment began.

After 12 years of artificial watershed acidification, basal area increment growth of black cherry, yellow poplar, and red maple trees was significantly reduced and soil fertility was diminished. Black cherry and yellow poplar wood chemistry data corroborated these observations.

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Chapter 1

INTRODUCTION

1.1. Air-Soil-Tree Relationships

The potential impacts of long-term atmospheric acidic deposition on forest ecosystems are of concern in the northeast U.S. Although the direct cause of tree decline and mortality over the last half century is controversial, it is now accepted that acidic deposition is a significant contributing factor. Several damaging abiotic and biotic stressors (e.g., disease, insect, drought, etc.) have received most of the blame for declines in tree growth. However, these factors may be ultimately responsible for mortality of trees already weakened by the effects of acidic deposition (McLaughlin, 1985; McLaughlin et al., 1996; Hendershot and Belanger, 1999; Swistock et al, 1999). Acidic deposition's role in tree dieback and mortality is evident because decline is usually highest on unglaciated, ridge-tops where the soils are sensitive to acidity and atmospheric deposition amounts are elevated (Joslin and Wolfe, 1992; Hendershot and Belanger, 1999; Swistock et al, 1999). The timing of red spruce decline was also coincident with increased acidic deposition (McLaughlin et al., 1987). Sharpe et al. (1999) observed that areas in Pennsylvania experiencing sugar maple decline were among the highest in the U.S. in loading of atmospheric deposition.

In the mid-Appalachians, certain regions are naturally acidic because the soil is derived from sandstones and shales with low carbonate content. The lack of carbonate content causes inadequate buffering and results in low levels of base saturation in the soil. Low base saturation is typically associated with soil acidity (Brady and Weil, 1996). In addition to natural acidification, atmospheric deposition of nitric and sulfuric acid in the region has contributed to increased leaching of base cations from soils, reduced concentrations of exchangeable Ca and Mg and increased leaching of Al to surface waters (Sharpe et al., 1984; DeWalle et al., 1985; Swistock et al., 1989; Drohan and

Sharpe, 1997; Lyon and Sharpe, 1999). Chemical interactions between these pollutants and soil can be extremely complex (Robarge and Johnson, 1992; Lotse, 1999). As the acid anions, sulfate (SO_4) and nitrate (NO_3), move through the soil, the initial response, if Ca and Mg are in good supply, may be enhanced fertility. However, as mobilization of cations continues, Ca and Mg, which are essential nutrients for proper tree growth, are leached from the system and eventually become depleted (Shortle et al., 1997; Edwards et al., 1999; DeWalle et al., 1999). During this process, the pH of the soil gradually declines and Al becomes more mobile (Cronan and Grigal, 1995; Lotse, 1999). Al, the third most abundant element in soils, is not usually a concern until pH drops below 5. At a pH of 5, Al compounds begin to dissolve and occur in soil solution (Runge, 1999). Once Al is mobilized, it outcompetes Ca and Mg for root exchange sites and further limits uptake of these nutrients (Reuss and Johnson, 1986; Cronan, 1991; Sparks, 1995). Al has the ability to cause permanent damage to plant cells; therefore, it is not easily assimilated by tree roots due to an exclusion mechanism in the apoplast (Sucoff et al., 1990; Cronan and Grigal, 1995).

Productivity of forest ecosystems depends on proper nutrient presence and availability. Ca is a key nutrient for proper plant growth. In trees, Ca aids in formation and stability of cell walls, activates membrane-bound enzymes, and regulates many responses of cells to stimuli (Cronan and Grigal, 1995). Although Ca deficits were not thought to limit forest growth in the past, studies now show that current rates of Ca depletion are high enough to negatively alter forest productivity. Shortle and Smith (1988) found that red spruce mortality was caused by Ca deficiencies induced by Al competition. Research on the Hubbard Brook Experimental Forest by Likens et al. (1998) showed that atmospheric acidic deposition caused significant depletion of the exchangeable pool of Ca in soils. Molar ratios of element concentrations have been used to identify the phases of nutrient enrichment and depletion in acidified soils (Bondietti et al. 1989). The effect of soil nutrient deficiencies on tree growth varies by species; however, severe deficiencies in Ca and Mg will adversely affect almost all tree species (Foy, 1984). Many tree species are adversely affected by increases in soil Al and decreases in soil Ca/Al ratios (Joslin and Wolfe, 1989). Much of the recent research on

Ca/Al ratios concluded that, the lower the ratio, the higher the risk of adverse effects on tree root growth. Cronan and Grigal (1995) observed that a Ca/Al ratio of 1.0 or less led to adverse effects in 50% of tree roots and a ratio of 0.4 increased the risk to 75%. Other research (Belanger et al., 1998) reported a 10% risk with a Ca/Al ratio of 4.0 and 50% risk of adverse effects to tree growth when the ratio was 0.8.

Although the effects of acidification on tree growth may be inferred by examining the chemical environment of soils, the growth and chemistry of trees must also be critically observed. A biological indicator is any living indicator that has the ability to express changes that occur in its immediate environment. Trees serve well as biological indicators because they are long lived and each year they develop annual growth increments (tree-rings), which are relatively easy to identify. The widths and quality of cells within each increment can be used to gain information about that tree's environment in any given year. Results from a study done on nine declining and non-declining sugar maple stands, indicated that visibly declining and apparently healthy trees on all sites had steadily decreasing diameter growth for approximately 30 years (Sharpe et al., 1999). Those results showed the importance of studying growth rates of declining trees, as well as those that are visibly "healthy". Another growth study demonstrated that in the last several decades there has been widespread decline of annual increment in red spruce trees (Bondietti et al., 1990). Once tree growth has been analyzed, the data can be compared to the soil chemical environment. A relationship was found between tree growth and soil chemistry by Swistock et al. (1999). They observed that sugar maple growth increased as the Ca/Al ratio in the soil increased.

While analysis of tree growth is important for recognizing declining stands, chemical analysis of plant material is needed to better determine causes of decline. Studies have shown that tree-ring chemistry can be a useful indicator of trace elements in the soil, record changes in air pollutant levels, and show chemical changes in the soil with fertility changes (DeWalle et al., 1995). Although Ca/Al molar ratios are useful indicators when working with soils, they are not useful in dendrochemistry because in trees Al uptake is blocked at the roots. Instead, Ca/Mn or Mg/Mn molar ratios may be used because Mn is an essential micronutrient readily taken up by trees (Kogelman and Sharpe, 1999). Manganese (Mn) behaves similarly to Al in that its availability to plants increases as pH decreases and it is not depleted as readily as base cations (Guyette et al., 1992; Kogelman and Sharpe, 1999). The potential use of Mn as an indicator for changes in tree chemistry lies in the fact that, unlike Al, it is a micronutrient that is assimilated more readily. DeWalle et al. (1999) demonstrated that base cation levels declined and Mn levels increased in the bolewood of yellow-poplar, black cherry, and red maple trees after eight years of acidification using ammonium sulfate treatments at the Fernow Experimental Forest in West Virginia. In other acidification trials, where ammonium sulfate was applied to soil to simulate atmospheric acidic deposition, strong declines in Ca/Al and Mg/Mn were exhibited in the bolewood of Japanese larch and tree heights and diameters were reduced (Pickens et al., 1995; DeWalle et al., 1999). Growth reductions in Japanese larch on this site were also reported by Kochenderfer et al. (1995).

1.2. Objectives

To better understand ecosystem response to acidic deposition, a study was initiated by the U.S. Forest Service Northeast Experimental Station on the Fernow Experimental Forest using ammonium sulfate treatments to accelerate the acidification process. The primary objectives of this study were: 1) to determine the effects of long-term artificial watershed acidification on the dendrochemistry of black cherry (*Prunus serotina* Ehrh.), yellow-poplar (*Liriodendron tulipifera* L.), and red maple (*Acer rubrum* L.). 2) to determine the impacts of artificial long-term acidification on radial and basal area growth rates of black cherry, yellow-poplar, and red maple trees.

Chapter 2

STUDY AREA AND METHODS

2.1. Study Area

Research was conducted on two watersheds within the Fernow Experimental Forest (FEF) in north central West Virginia (39°3'15"N, 79°41'15"W) (Figure 2.1.1.). The 1900 ha FEF lies in the Allegheny Mountain section of the unglaciated Allegheny Plateau. The climate is cool and rainy with an average annual temperature of approximately 48°F and an average precipitation of about 147 cm annually. The frost free season lasts about 145 days (U.S. Forest Service, 2001). Soils on study watersheds are generally about one meter deep and of the Calvin series (loamy-skeletal, mixed, mesic, Typic Dystrochrepts) derived from sandstone and shale (Gilliam et al., 1996).

A watershed acidification study was initiated in 1989 on watershed three (WS3) and an adjacent control site, watershed seven (WS7). Granular ammonium sulfate [$(NH_4)_2SO_4$] applications began on WS3 in January 1989 and have continued to be applied at twice the amount of average annual atmospheric deposition of nitrogen (N) and sulfur (S) occurring in that area. March and November applications were 33.6 $kg \cdot ha^{-1}$ and July applications were 100.8 $kg \cdot ha^{-1}$. Acidification effects on soil and tree-ring chemistry of black cherry, yellow-poplar and red maple trees were studied after four and eight years of treatment; however, growth rates were not assessed. This study was conducted in July of 2000, twelve years after the first treatment. It replicated the previous work completed after four and eight years of treatment and analyzed tree growth.

The treatment and control watersheds were selected for this study due to their adjacent positions and their similarity in soils, species composition, and stand age (Tables 2.1.1. and 2.1.2.).

Table 2.1.1. Characteristics of treatment (WS3) and control (WS7) watersheds on the Fernow Experimental Forest, West Virginia

Characteristic	WS3	WS7
Area (ha)	34.3	24.2
Aspect	S	ENE
Elevation Range (m)	735-860	725-855
Stand Age (yr)	30	30
Dominant Tree Species	*Prunus serotina*	*Prunus serotina*
	Liriodendron tulipifera	*Liriodendron tulipifera*
Soils	Calvin silt loam	Calvin silt loam

Sources: DeWalle et al., 1995; Gilliam and Adams, 1995

Table 2.1.2. Comparison of treatment and land use history for treatment (WS3) and control (WS7) watersheds on the Fernow Experimental Forest, West Virginia.

Watershed	Treatments	Dates
WS3	Weir Installation	5/51
	Intensive selection cut	10/58-2/59
	Repeated cut	9/63-10/63
	Patch cutting w/ herbicide	7/68-8/68
	Clearcut, left stream buffer	7/69-5/70
	Cut buffer, clear channel	11/72
	Ammonium sulfate treatment initiated	1/89
WS7	Weir Installation	11/56
	Upper 12.1 ha clearcut	11/63-3/64
	Herbicide upper cut	5/64-10/69
	Lower 12.1 ha clearcut	10/66-3/67
	Herbicide lower cut	5/67-10/69

Sources: Adams et al., 1994; DeWalle et al., 1995

2.2. Methods

2.2.1. Soil Sampling and Analysis

To determine the effect of the ammonium sulfate treatment on soil fertility, soil samples were taken in July 2000. Soil was sampled from the O, A, and B horizons around sample tree locations on WS3 and WS7 from a total of 20 shallow, hand excavated soil pits (10 on each watershed). Soil samples were placed in zip-lock storage bags. Samples were air dried and sent to Agricultural Analytical Services Laboratory at the Pennsylvania State University for chemical analysis. Standard analysis of soil samples included: pH, CEC, exchangeable base cations, and soil acidity using the Mehlich 3 test (Mehlich, 1984). An Al stress test was also performed using a 0.01 M $SrCl_2$ of Ca and Al and a molar Ca/Al ratio was calculated from the data. Extraction with 0.01 M $SrCl_2$ estimates the plant available fraction of Al (Joslin and Wolfe, 1989). Results obtained were analyzed using a simple t-test (Minitab Inc., 2000) and compared by horizon between the treatment and control watersheds.

Soil data were also compared to soil data derived from samples taken on the same watersheds in May 1995 (Tepp, 1995). However, due to different methods used to analyze samples, only the pH, CEC, Ca, Mg, P, and K data are comparable.

2.2.2. Wood Core Sampling and Analysis

To study the continuing effects of watershed acidification on black cherry, yellow-poplar and red maple trees after 12 years of treatment, tree-core samples were obtained in July 2000, from ten mature trees of each species on WS3 and WS7. For chemical analysis, each tree was cored twice at breast height with a 4-mm diameter increment borer. Sterilized gloves were worn throughout the coring process. Extracted cores were rinsed with deionized water, placed into plastic straws, and frozen until time of analysis. Later, the cores taken for chemical analysis were removed individually from the freezer and separated into six sample periods by counting annual growth rings. Sample periods were:

Treatment Period III	1997-2000
Treatment Period II	1993-1996
Treatment Period I	1989-1992
Pre-Treatment I	1986-1988
Pre-Treatment II	1981-1985
Pre-Treatment III	1976-1980

Analysis was conducted for Ca, Mg, Sr, P, K, Na, Mn, Al, Fe, Cu, B, and Zn using inductively-coupled plasma emission spectroscopy (ICP) at the Agricultural Analytical Services Laboratory on the Penn State Campus using procedures of Dahlquist and Knoll (1978). Results obtained from the laboratory were analyzed using a simple t-test (Minitab Inc., 2000) and compared to similar wood chemistry data reported by Tepp (1995).

To analyze the treatment effects on the growth rates of the three tree species, an additional core was taken at breast height from each tree. Cores for analysis of growth rate were removed without concern for chemical contamination. These cores were also placed in straws; however, the straws were later opened and the cores allowed to air dry. After the growth cores were dried, they were mounted on grooved hardwood blocks and sanded with 220, 320, 400, and 600 grit sand paper. They were then studied through a binocular microscope for crossdating purposes and the position of each growth ring was digitized to the nearest 0.01 mm using a high resolution scanner and WinDENDRO v. 6.5d manufactured by Regent Instruments Inc.(Quebec, Canada). Ring width series were compared graphically and statistically between WS3 and WS7. To eliminate other factors that may have contributed to growth differences between sites, a radial growth ratio was determined for each tree based on its average growth prior to the treatment year. For each individual tree, the radial growth for each year after the treatment period was divided by the average growth rate for 14 years prior to the treatment period. These ratios were then analyzed using a simple t-test (Minitab Inc., 2000).

Tree-ring widths were converted to basal area increment (BAI) to remove any variation in radial growth as a result of increasing tree circumference (Kolb and McCormick, 1993; Swistock et al., 1999). BAI was computed for all sampled trees on WS3 and WS7 using ring widths determined from the growth analysis, the diameter at breast height (DBH), and bark thickness measured in the field. Wood diameter at breast height (DBH_w) was calculated as:

$$DBH_w = DBH_F - 2B$$

where DBH_F is the diameter at breast height measured in the field in inchesand B is the average bark thickness in inches. Total wood radius (R_w) in millimeters is then:

$$R_w = 0.5\ (25.4 * DBH_w)$$

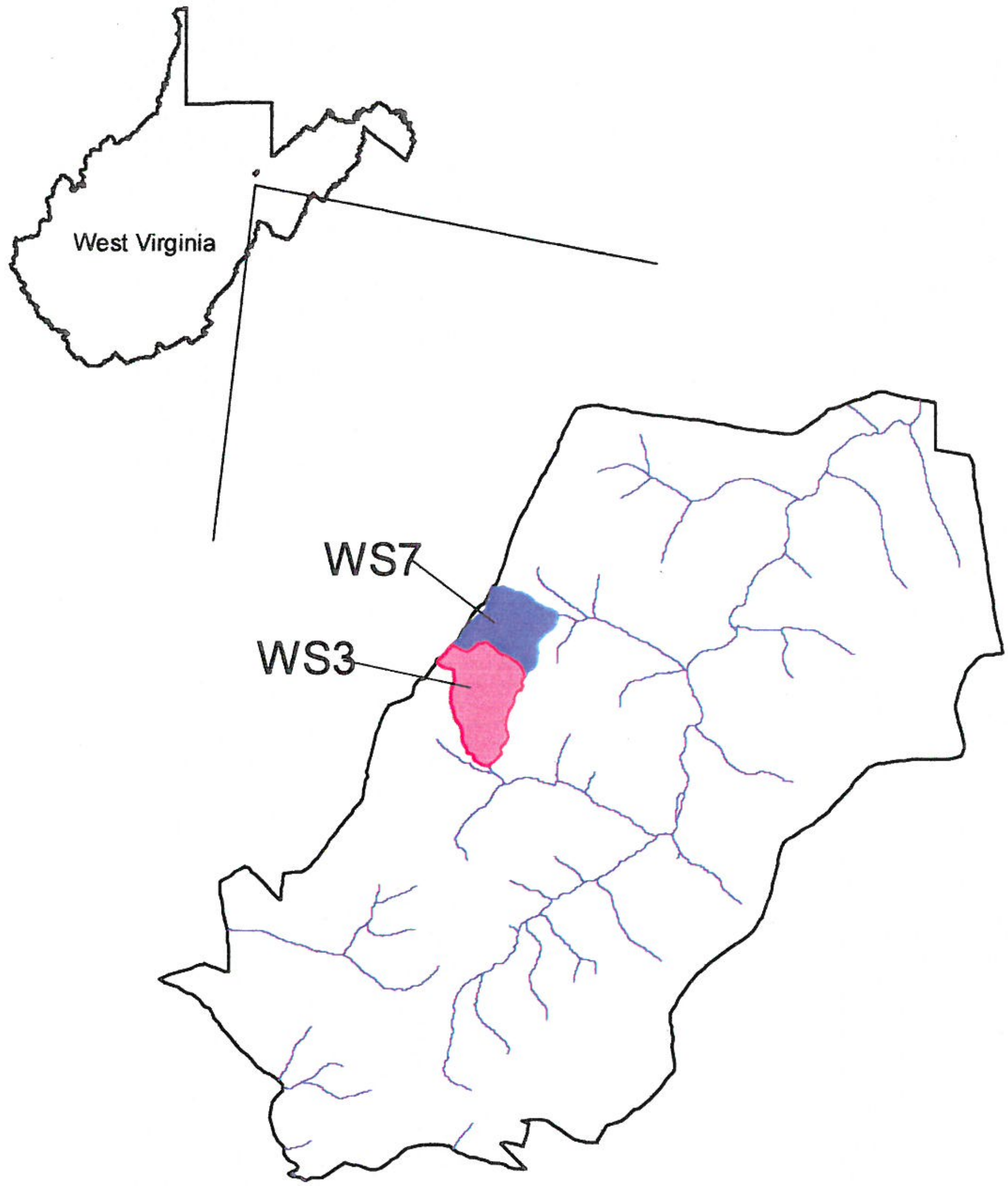
where DBH_w is the wood diameter at breast height in inches. BAI is calculated from the ring width (W) and the bolewood radius (R). The BAI calculation is derived from an equation of the difference in area between two circles and is calculated from the outside year, working inward. The units for BAI are in square millimeters. BAI for year, N, is:

$$BAI_N = \pi\ (R_N^2 - R_{N-1}^2)$$

where

$$R_{N-1} = R_N - W_N$$

Figure 2.1.1. Fernow Experimental Forest located in north central West Virginia.



Fernow Experimental Forest

Chapter 3

RESULTS AND DISCUSSION

3.1. Soil Chemistry

Mean soil pH, CEC, acidity, and ion concentrations for the control (WS7) and the treatment (WS3) watersheds are given in Table 3.1.1. Some significant differences between the two study watersheds were found in data from all three soil horizons. WS3 had significantly lower pH in the O, A, and B horizons, which is consistent with the findings of Tepp (1995). However, in the past six years, the pH of both watersheds decreased (it is important to note that the decrease in treatment being twice the decrease experienced on the control). Although WS3 received ammonium sulfate treatments for 12 years, both watersheds receive atmospheric deposition inputs and both were disturbed prior to the commencement of this study. This could explain why the pH is lower on both watersheds at the present time compared to six years ago. The significant difference in pH between watersheds in the past and present study is evidence that the ammonium sulfate treatment accelerated the acidification process. Since the pH was significantly lower on the treated watershed, it may be expected that plant available Al concentrations (0.01 M $SrCl_2$) would also be elevated on this watershed. Results showed that Al was significantly higher in all three horizons on the treated watershed compared to the control (Table 3.1.2.).

Exchangeable Ca was lower on WS3 versus WS7; with significant differences in the O and B horizons (Table 3.1.1.). Exchangeable Ca increased slightly on both watersheds when compared to the 1995 data; however, it was minor and probably explained by the lack of precise duplication of the 1995 sampling methods and locations. Exchangeable Mg, P, and K were not significantly different in the A and B horizons between WS3 and WS7, and were very similar to the data of Tepp (1995).

Table 3.1.1. Chemistry of soil samples (n=10) taken in the O, A, and B horizons on treatment (WS3) and control (WS7) watersheds in July 2000. Tepp's (1995) soil data on WS3 and WS7 taken in May 1995 was included for comparison purposes. Mean (M) pH, concentrations (mg/kg) of exchangeable Ca, Mg, P, K, and (meq/100g) of CEC and acidity are shown with their associated standard deviation (s). * represents significance at $\alpha \leq 0.1$ and ** represents significance at $\alpha \leq 0.05$. A (-) indicates that no data were available.

			Present Study (2000)		Tepp's Study (1995)	
Parameter	Statistic	Horizon	WS3 2000	WS7 2000	WS3 1995	WS7 1995
pH	M	O	3.77*	4.46	-	-
	s		0.13	0.42	-	-
	M	A	3.91**	4.47	4.29**	4.68
	s		0.15	0.27	0.2	0.4
	M	B	4.28**	4.62	4.64**	4.85
	s		0.14	0.20	0.13	0.23
CEC	M	O	16.38	15.82	-	-
	s		1.22	1.68	-	-
	M	A	15.51	14.72	14.3	14.6
	s		1.13	2.46	2.88	1.83
	M	B	12.08	11.46	8.42**	10.01
	s		2.75	2.21	1.62	2.95
Ca	M	O	300.80*	536.00	-	-
	s		73.50	381.00	-	-
	M	A	114.80	160.00	106.70**	257.8
	s		13.60	107.00	42.7	364.3
	M	B	86.10*	100.40	56.9	119.3
	s		11.10	26.00	27	198.2
Mg	M	O	36.50**	61.40	-	-
	s		5.76	34.50	-	-
	M	A	24.80	28.30	25.02	33.63
	s		1.62	10.50	8.96	24.93
	M	B	20.20	21.10	18.77	25.81
	s		2.04	2.92	3.91	23.76
P	M	O	12.10**	23.00	-	-
	s		3.75	10.60	-	-
	M	A	5.60**	15.10	10.38**	16.82
	s		1.26	10.20	8.8	8.21
	M	B	5.80	5.30	4.14**	6.52
	s		2.35	2.26	1.84	4.65
K	M	O	59.0**	91.70	-	-
	s		16.20	35.30	-	-
	M	A	41.30	51.60	64.59**	77.42
	s		9.51	22.30	15.6	26.4
	M	B	32.30	33.60	32.84**	42.7
	s		6.77	10.00	9.24	17
Acidity	M	O	17.13**	13.13	-	-
	s		3.30	4.17	-	-
	M	A	17.38**	13.99	-	-
	s		3.05	2.66	-	-
	M	B	11.67	10.67	-	-

Results for the 0.01 M $SrCl_2$ extractions (plant available) of Al and Ca revealed that WS3 had significantly lower Ca/Al molar ratios than WS7 in all three soil horizons (Table 3.1.2.). There were no soil samples with a Ca/Al of 1 or less in the O horizon of WS3. Seventy percent of soil samples from the A horizon on WS3 had a Ca/Al ratio of 1 or less. Ninety percent of soil samples from the B horizon on WS3 had a Ca/Al ratio of 1 or less. Tree roots located in the A and B soil horizons of WS3 are likely to be adversely effected by the relatively low Ca/Al ratios (Cronan and Grigal, 1995).

Table 3.1.2. Plant-available Al and Ca from soil samples taken in the O, A, and B horizons on treatment (WS3) and control (WS7) watersheds. Mean (M) concentrations (mg/kg) of Al and Ca are shown with their associated standard deviations. A Ca/Al molar ratio is also shown with its associated standard deviation (s). The symbol * represents significance at $\alpha \leq 0.1$ and ** represents significance at $\alpha \leq 0.05$.

Paramete	Statistic	Horizon	WS3	WS7
Ca	M	O	90.50	118.70
	s		31.40	60.90
	M	A	54.90*	83.90
	s		18.70	50.80
	M	B	28.95**	43.30
	s		4.89	19.20
Al	M	O	8.46**	3.61
	s		3.09	2.53
	M	A	37.65**	17.49
	s		9.99	9.19
	M	B	26.21**	15.79
	s		6.28	5.34
Ca/Al	M	O	9.90*	47.50
	s		10.20	73.70
	M	A	1.02*	5.30
	s		0.38	7.87
	M	B	0.77**	2.31
	s		0.24	2.09

3.2. Bolewood Chemistry

Black cherry has a moderately wide sapwood zone; however, timing of response to acidification treatments was still difficult to comprehend. Data from summer 2000 showed that Ca had significantly higher concentrations in WS7 (control) than WS3 (treatment) in wood formed in 1989 to 2000 (Figure 3.2.1.). These results were interesting because dendrochemical work done by Tepp (1995) on the same watersheds observed Ca in 1976 to1992 be significantly higher on WS3 compared to WS7 in wood formed in 1989 to 1992. These conflicting results can be explained by a combination of the mobilization-depletion theory and knowledge of black cherry's sap-conducting tissue. The mobilization-depletion theory, demonstrated in many wood chemistry studies, explains that following prolonged soil acidification, base cations are temporarily mobilized within the soil complex making them more available for tree root uptake and leaching (DeWalle et al., 1991). This mobilization is followed by a depletion phase, where base cations depleted by leaching are also out-competed for root exchange sites by the increasingly available Al^{3+}. Tepp's work was probably done during the mobilization phase since treatment was initiated in January of 1989, while the current research demonstrated that these trees were in the depletion phase at least from 1997 to 2000. The sap-conducting tissue within these trees may have redistributed some of the nutrients, making it seem as though they were in the depletion phase for a longer period of time. If sampling occurred while the trees were actively conducting sap, it would be impossible to know the absolute element concentrations for each time segment. Mn was the only other element that was easily understood in the results obtained for black cherry trees (Figure 3.2.2.). Data showed that Mn was significantly higher in black cherry trees on WS3 (treatment) compared to WS7 (control) from 1989 to 2000. This was expected since Mn also out-competes Ca and/or Mg for root exchange sites and is more readily absorbed into tree roots. Results for P, K, Fe, Cu, B, Zn, and Na in black cherry were not significantly different between treatment and control sites. Mg, Al, and Sr had mixed results and were not completely understood.

Figure 3.2.1. Mean Ca (ug/g) concentrations in black cherry trees sampled on WS3 and WS7 in 2000. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

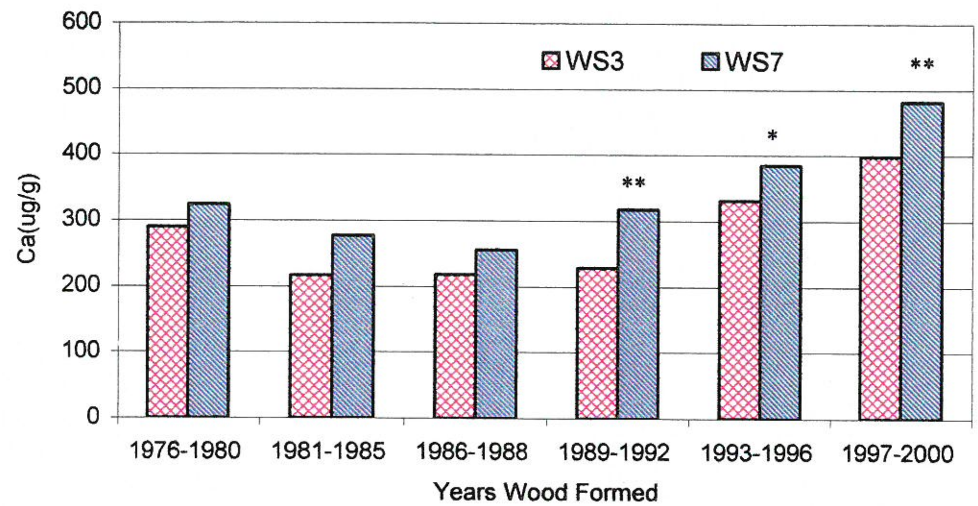


Figure 3.2.2. Mean Mn (ug/g) concentrations in black cherry trees sampled on WS3 and WS7 in 2000. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

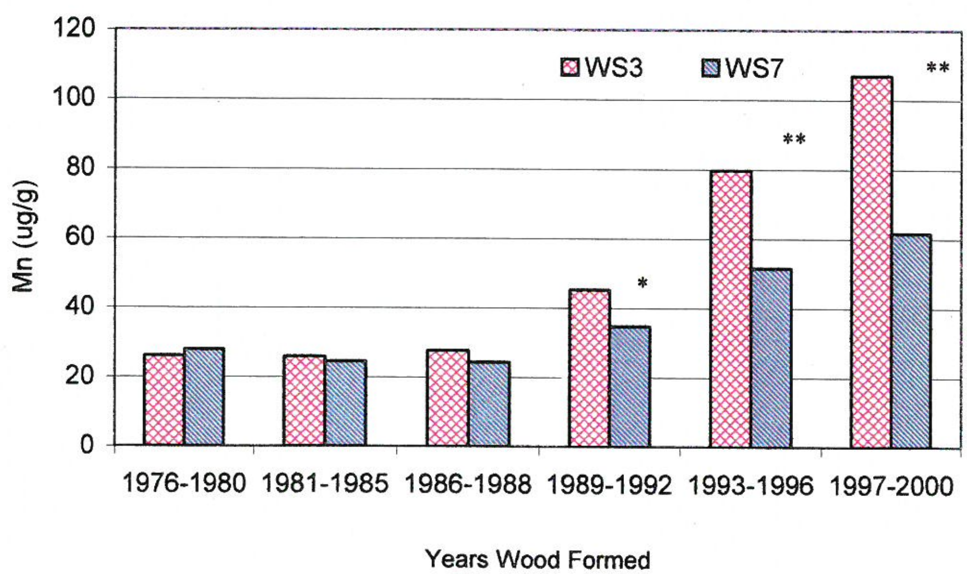
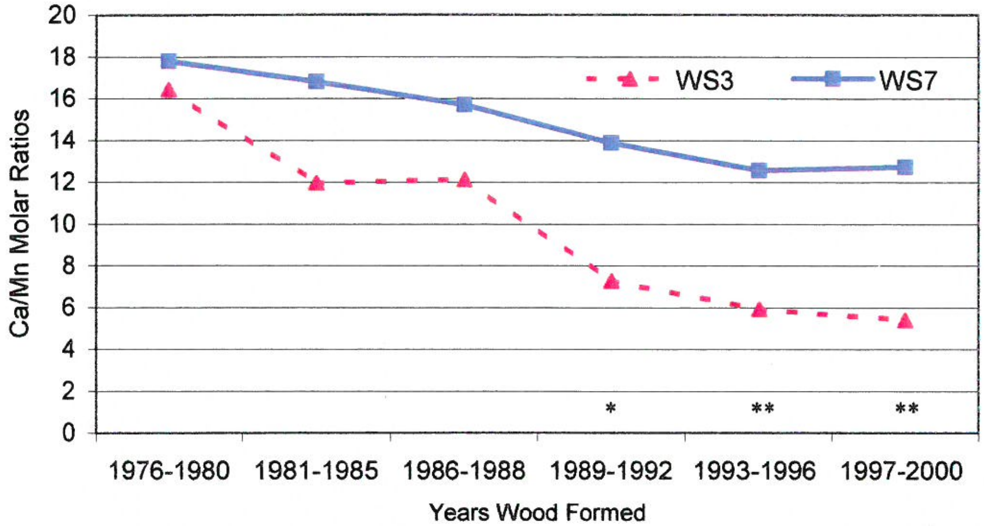
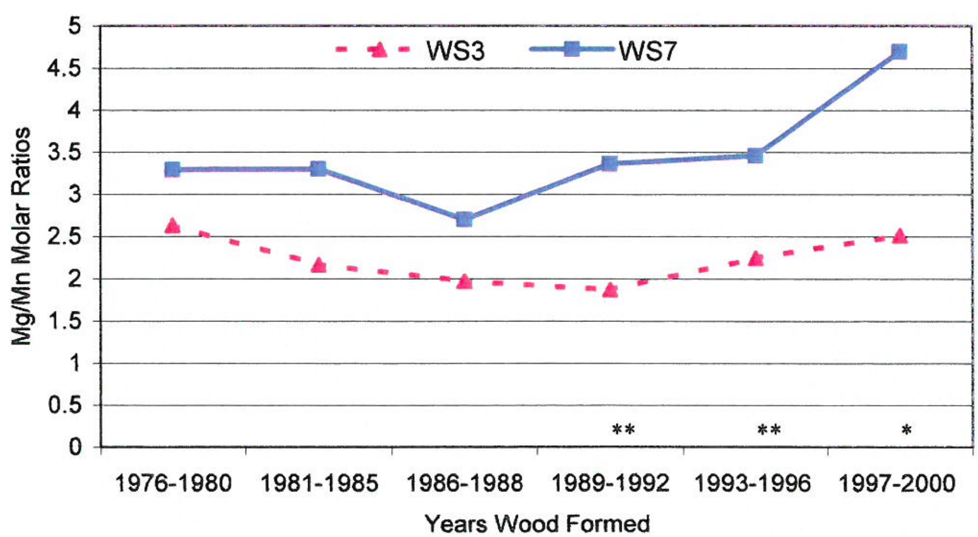


Figure 3.2.3. Mean Ca/Mn molar ratio concentrations in black cherry tree rings on treated (WS3) and control (WS7) watersheds in 2000. Significance is noted by ** ($\alpha \leq$ 0.05) and * ($\alpha \leq 0.10$).



Results for both Ca/Mn and Mg/Mn molar ratios in black cherry were significantly lower in the treated watershed (WS3) compared to the control watershed (WS7) from 1989 through 2000 (Figure 3.2.3. and 3.2.4.). These results would indicate That WS3 black cherry trees are at greater risk of advice effects than WS7 black cherry trees.

Figure 3.2.4. Mean Mg/Mn molar ratio concentrations in black cherry tree rings on treated (WS3) and control (WS7) watersheds. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).



Overall wood chemistry results for yellow-poplar were similar to those of black cherry. Yellow-poplar Ca concentrations were significantly lower in WS3 than WS7 in wood formed in 1981 through 2000 (Figure 3.2.5.). It is almost certain that sap-conducting tissue played a part in redistributing Ca since Tepp's research on the same watersheds gave conflicting data. His work showed that the treated watershed (WS3) had increased Ca when compared to the control watershed (WS7) from 1981 through 1992. This comparison of present and past data on the same tree species in the same watersheds supports that mobilization and depletion of Ca did occur in these trees; however, Mn also showed an obvious treatment effect having significantly higher concentrations on WS3 compared to WS7 in all years (Figure 3.2.6.). Tepp again showed the opposite with Mn concentrations being lower in WS3 compared to WS7. These inconsistencies actually substantiate the sapflow theory. Yellow-poplar results for Al were unlike the other two tree species completely. Raw data demonstrated elevated Al concentrations in all years in both watersheds. Although the concentrations were not significantly different between WS3 and WS7, Al concentrations were consistently higher in yellow-poplar than in black cherry or red maple wood. This suggests that yellow-poplar's exclusion mechanism for Al in the apoplast may not work as efficiently as in other tree species and further study should be done. Results for P, K, Fe, Cu, B, Zn, and Na in yellow-poplar were not significantly different between control and treatment watersheds while Mg and Sr, results were variable.

The sapwood zone in yellow-poplar trees is much greater than that of black cherry, making it virtually impossible to determine the mobilization and depletion phases by wood chemistry techniques where sapwood is used. This makes using young yellow-poplar for dendrochemical studies a disadvantage over other species with less sap-conducting tissue.

Figure 3.2.5. Mean Ca (ug/g) concentrations in yellow-poplar trees on WS3 and WS7 in 2000. Significance is noted by ** (α ≤ 0.05) and * (α ≤ 0.10).

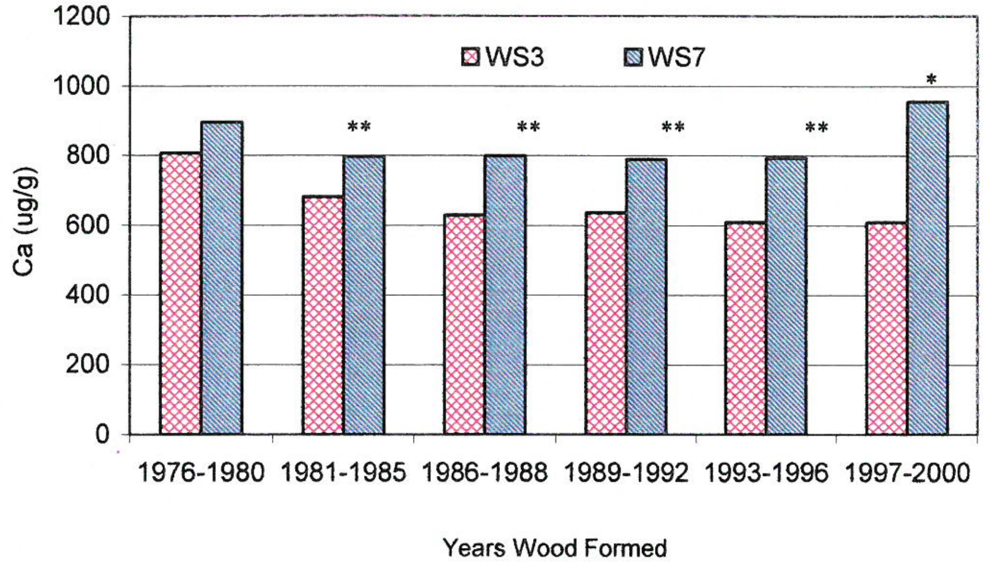
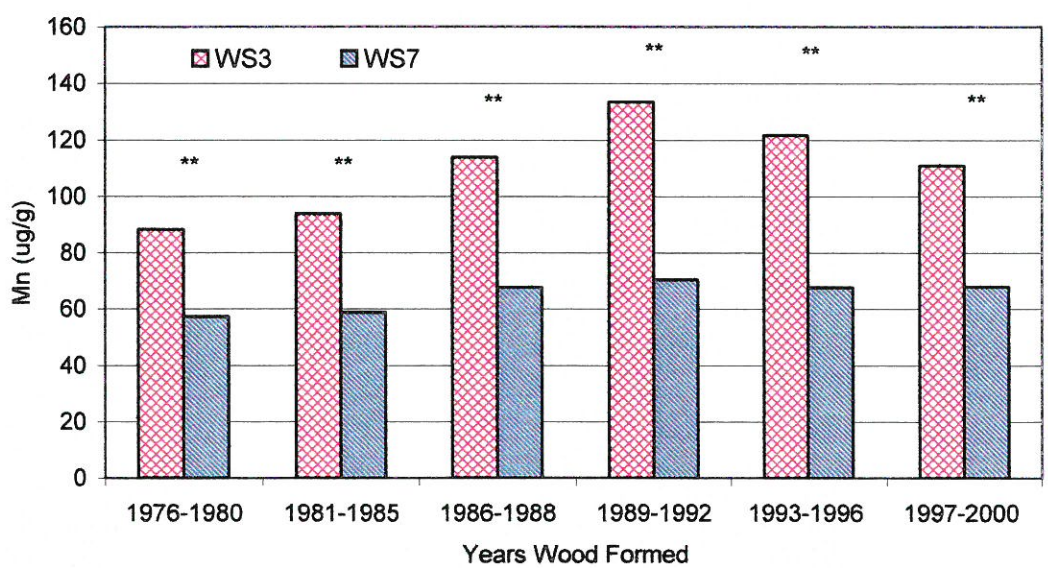


Figure 3.2.6. Mean Mn (ug/g) concentrations in yellow-poplar trees on WS3 and WS7 in 2000. Significance is noted by ** (α ≤ 0.05) and * (α ≤ 0.10).



Both Ca/Mn and Mg/Mn molar ratios in yellow-poplar in 2000 were significantly lower in the treated watershed (WS3) compared to the control watershed (WS7) in wood formed in 1976 through 2000 (Figure 3.2.7. and 3.2.8.). These results would indicate that WS3 yellow-poplar trees are at greater risk of adverse effects than WS7 yellow-poplar trees.

Wood chemistry results for red maple trees in 2000 after 12 years of treatment were much different than with the other two tree species studied. Ca, Mn, Mg, Al, and Sr results were varied and higher concentrations generally occurred in wood on WS7 than WS3. Results for P, K, Fe, Cu, B, Zn, and Na in red maple were similar to the other two species in that no significant difference between the control and treatment watersheds was detected. Tepp (1995) found similar results, indicating that red maple did not respond as readily to acidification treatments as black cherry and yellow-poplar. Demchik and Sharpe (1999) demonstrated that red maple was relatively insensitive to acidified soils and Adams et al. (1995) found that red maples have the ability to absorb nutrients through the foliage in greater amounts than other tree species.

Ca/Mn molar ratios in red maple on WS3 were consistently below WS7 in 2000, but not significantly in any year segment (Figure 3.2.9.). Red maple Mg/Mn molar ratios showed a similar effect as Ca/Mn, except there was a significant difference between treatment and control in the oldest four segments (Figure 3.2.10.).

Figure 3.2.7. Mean Ca/Mn molar ratio concentrations in yellow-poplar tree rings on treated (WS3) and control (WS7) watersheds. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

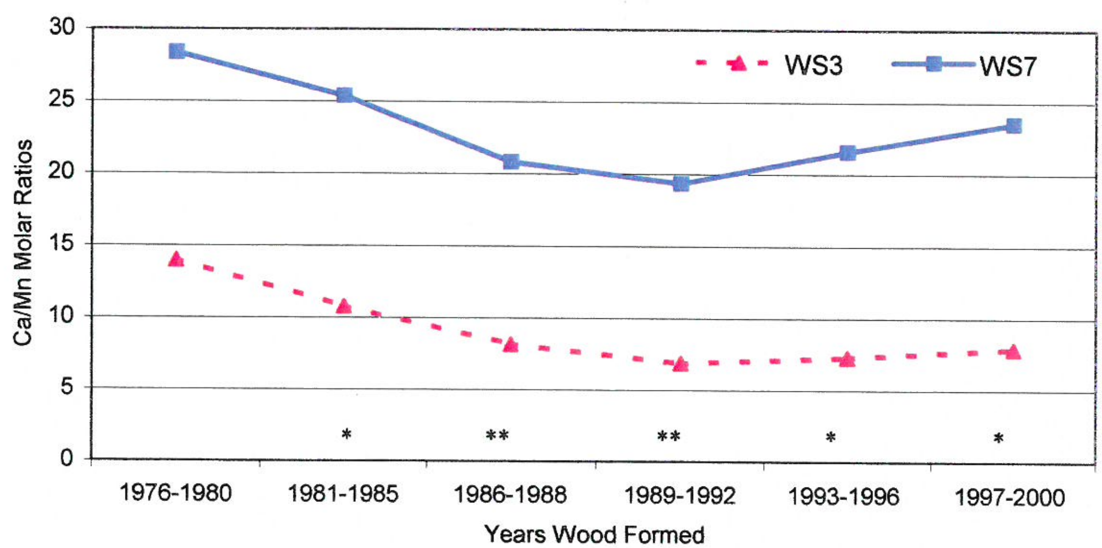


Figure 3.2.8. Mean Mg/Mn molar ratio concentrations in yellow-poplar tree rings on treated (WS3) and control (WS7) watersheds. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

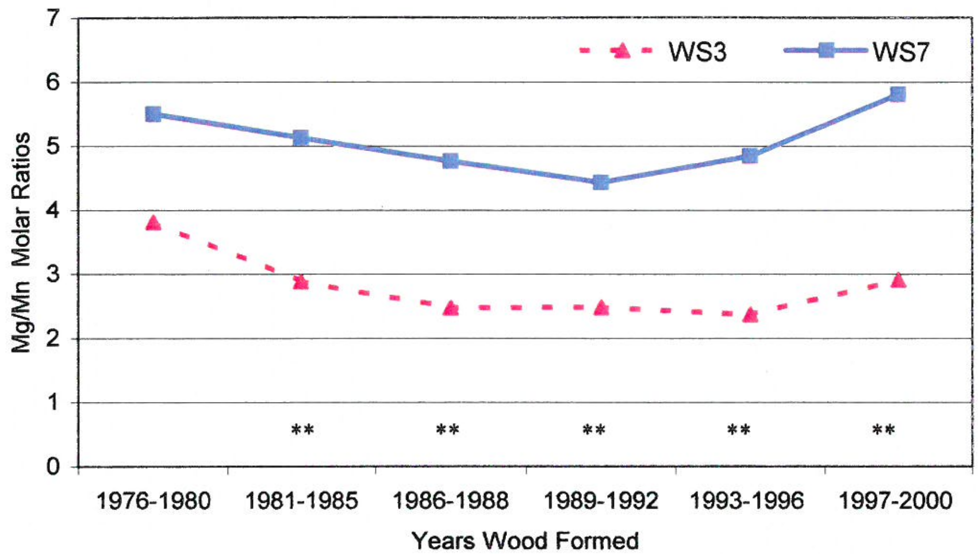


Figure 3.2.9. Mean Ca/Mn molar ratio concentrations in red maple tree rings on treated (WS3) and control (WS7) watersheds in 2000. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

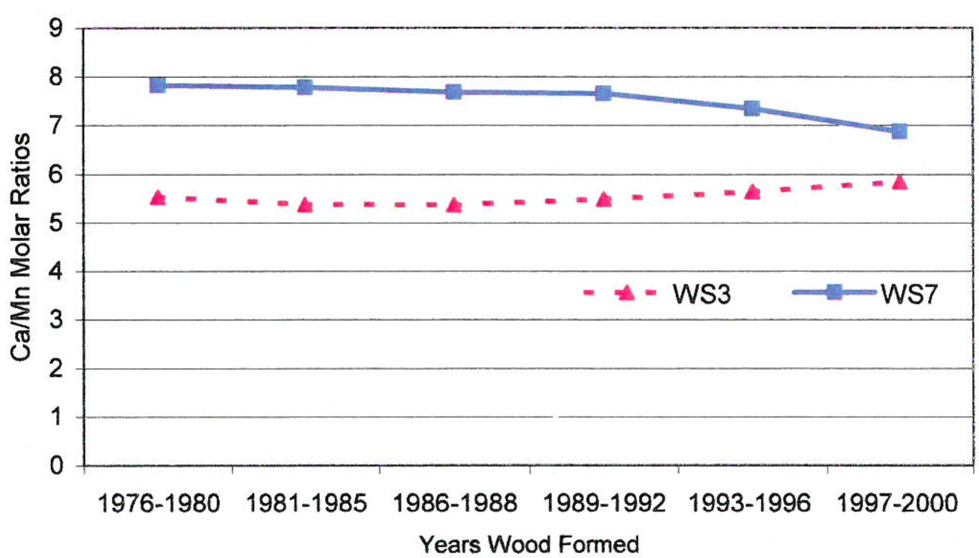
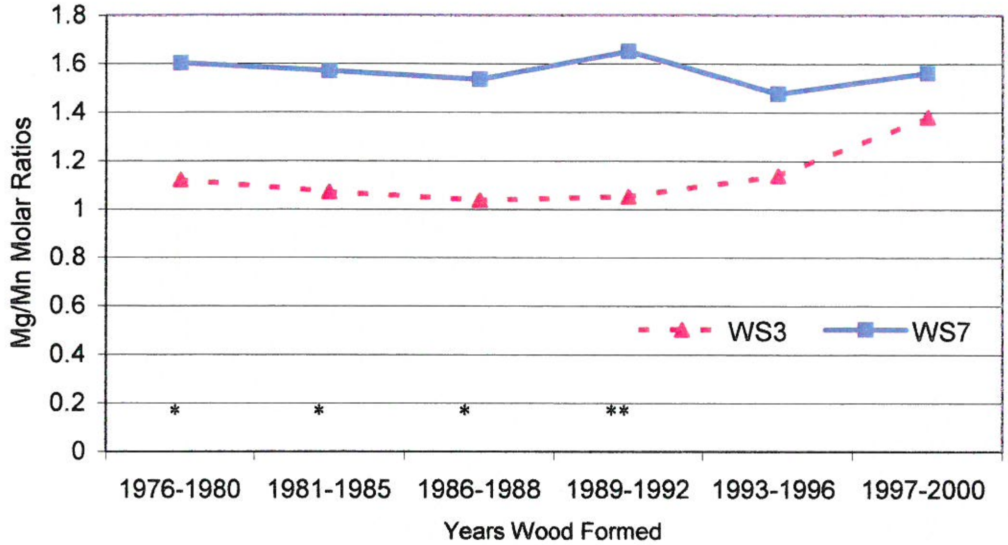


Figure 3.2.10. Mean Mg/Mn molar ratio concentrations in red maple tree rings on treated (WS3) and control (WS7) watersheds in 2000. Significance is noted by ** ($\alpha \le 0.05$) and * ($\alpha \le 0.10$).



It was difficult to accurately determine the exact time of treatment effect in all species studied. Varying widths in sap-conducting tissue and the possibility of radial translocation of elements, made it extremely difficult to fully understand the wood chemistry of black cherry, yellow-poplar, and red maple trees. In particular, red maple trees should not be used when analyzing bolewood chemistry.

Radial Tree Growth

Results from analysis of radial growth were quite different between the three tree species tested. Black cherry trees on the treatment watershed (WS3) grew significantly better than the trees on the control watershed (WS7) from four to seven years after treatment. In the eighth year their growth was similar to each other, and from year nine through eleven after treatment, WS3 black cherry trees grew significantly slower than on WS7 (Figure 3.3.1.). The increase in growth in years four through seven after treatment on WS3 trees can be explained by a temporary mobilization effect of Ca and Mg. These results are consistent with DeWalle et al., 1991 and DeWalle et al. (1999). The initial response in soils after the onset of acidification is an increase in availability of Ca and Mg, which leads to increased growth. As these nutrients are depleted by leaching, Al becomes more mobile and growth will decline. The decrease in growth of WS3 black cherry trees in years eight through eleven appear to fit the mobilization/depletion theory.

Yellow-poplar trees behaved similarly to black cherry trees on both watersheds. There was better growth on the treatment trees in years five through seven after treatment; however the difference was not significant. Those same trees grew significantly slower than the control trees in years nine through twelve (Figure 3.3.2.). These results can also be explained by the mobilization and depletion theory.

Red maple trees did not respond like black cherry or yellow-poplar trees on either watershed. Although the trees on WS3 grew significantly slower than on WS7 in years ten through twelve, WS3 trees grew more slowly in all years after treatment (Figure 3.3.3.). The difference in growth appeared to increase with years after treatment possibly indicating a treatment effect.

Figure 3.3.1. Radial growth rates in black cherry trees on the treatment (WS3) and control (WS7) watersheds. The treatment year was 1989 and is indicated with an arrow. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

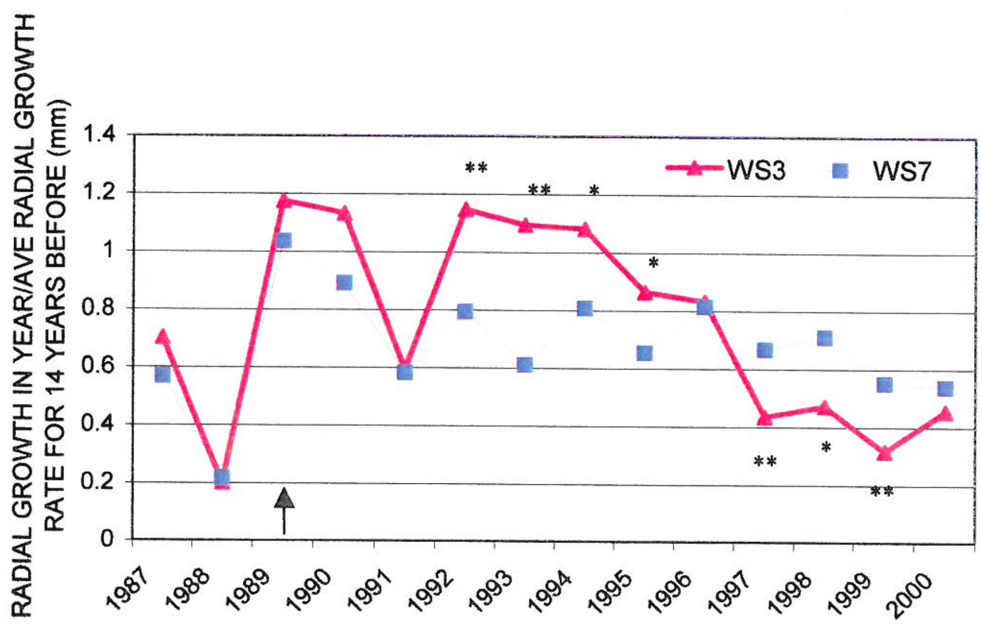


Figure 3.3.2. Radial growth rates in yellow-poplar trees on the treatment (WS3) and control (WS7) watersheds. The treatment year was 1989 and is indicated with an arrow. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).

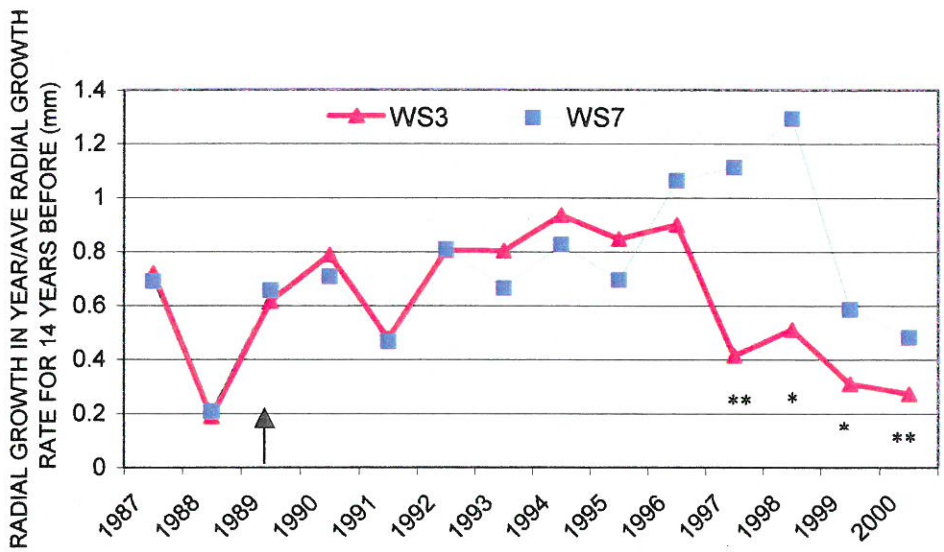
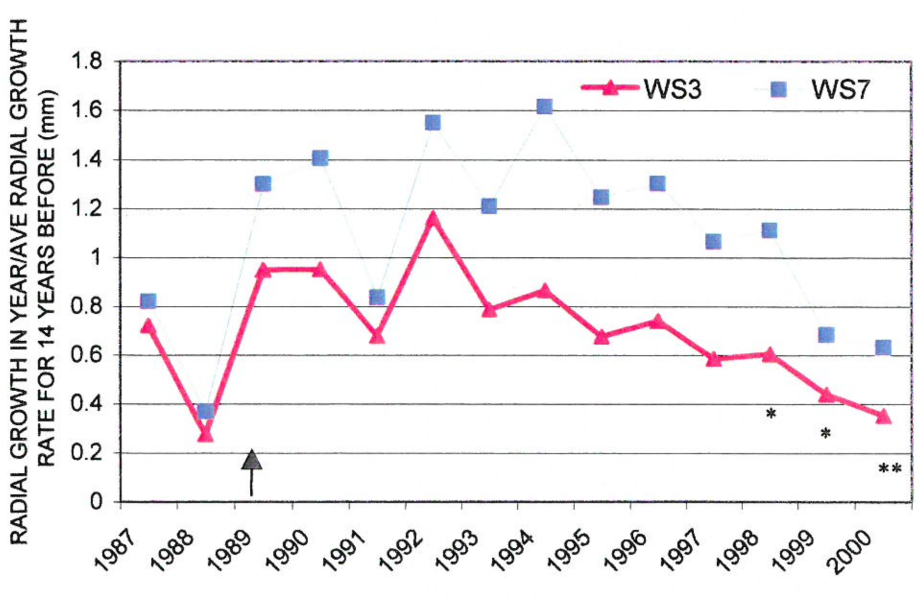


Figure 3.3.3. Radial growth rates in red maple trees on the treatment (WS3) and control (WS7) watersheds. The treatment year was 1989 and is indicated with an arrow. Significance is noted by ** ($\alpha \leq 0.05$) and * ($\alpha \leq 0.10$).



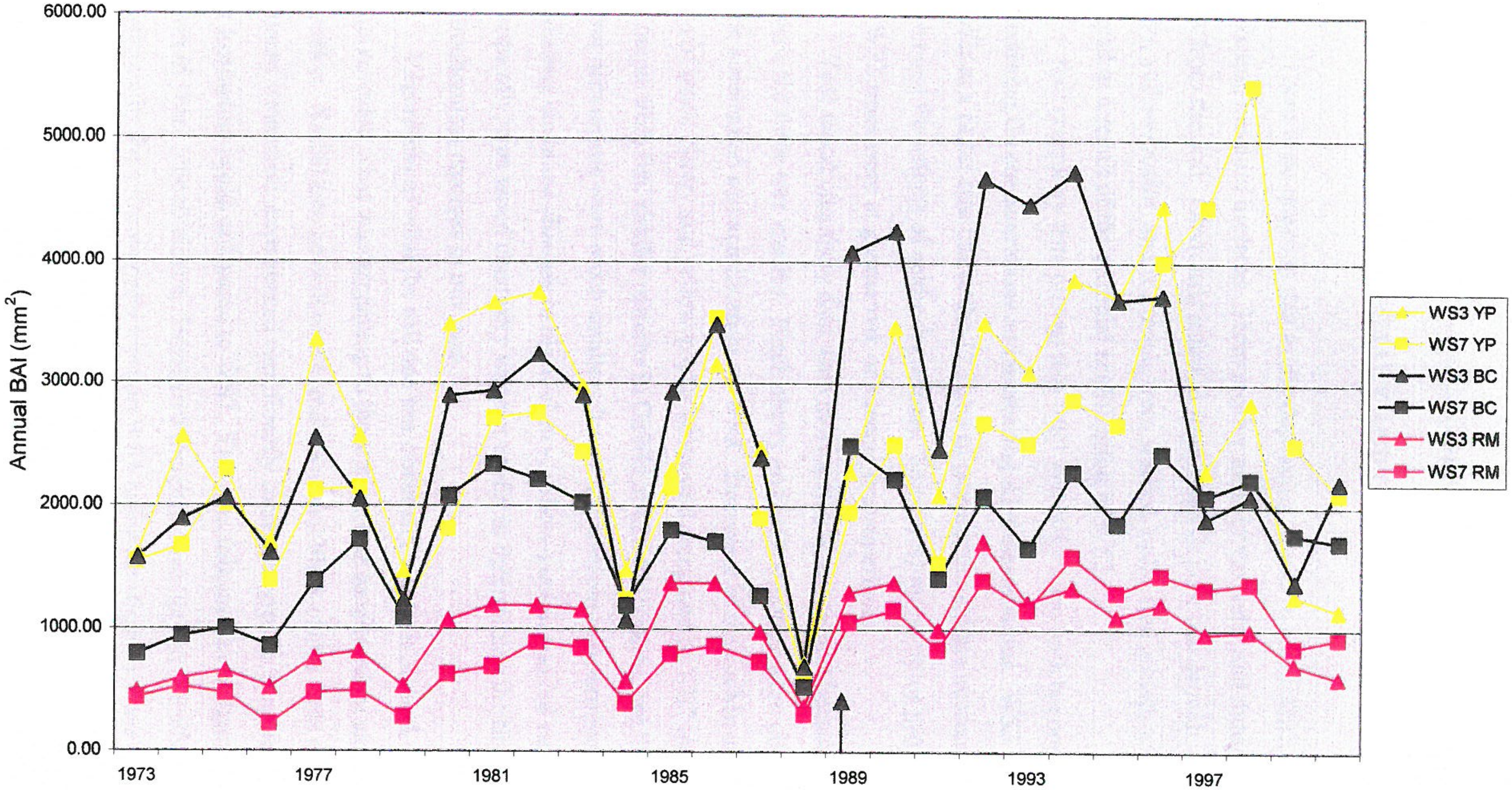
Results for basal area increment (BAI) of each species, supported the results obtained from the growth study. Black cherry trees on WS3 grew slightly better than the trees on WS7 for most of their life. In 1992, the difference between growth on the two sites became much greater, with WS3 having better growth than any previous year. Abruptly in 1997, WS3 trees had a substantial decrease in growth and dropped below WS7 trees (Figure 3.3.4.).

BAI for yellow-poplar trees was also consistent with radial growth. Growth of yellow-poplar trees on WS3 and WS7 was similar throughout most of their life; however, in 1997, WS3 trees dropped below WS7 trees in growth (Figure 3.3.4.). Yellow-poplar tree growth trends seem to be similar to trends in black cherry growth on the control and treatment watersheds.

Although diameter growth data for red maple trees was inconclusive, BAI data indicated that there was a treatment effect. These results showed red maple trees on WS3 had elevated growth for every year from 1973-1993. After that year, trees on WS3 decreased in growth enough to drop below trees on WS7 through year 2000 (Figure 3.3.4.). Although a mobilization effect was not evident in diameter or BAI results, treatment trees also dropped below control trees as with the other two species. It has been observed from other studies that red maple is one of several tree species that is relatively tolerant to acidified soils (Tepp, 1995; Demchik and Sharpe, 1999); consequently, some difference in response to the acidification treatments was not unexpected. However, results show that even red maple growth can be affected.

Analysis of tree growth for the selected tree species indicated that all three trees responded to the acidification treatment with declining growth in the last four or five years.

Figure 3.3.4. Mean annual basal area increment (BAI) for black cherry (black line), yellow-poplar (yellow line), and red maple (red line) trees on WS3 and WS7. Triangles represent the treatment watershed (WS3) and squares represent the control watershed (WS7). The treatment year is indicated by an arrow.



Chapter 4

SUMMARY AND CONCLUSIONS

There is no question that acidic deposition results in soil acidification. Soils are the rooting medium for trees. Trees receive most of the water and nutrients they need to grow from the soil. Obviously infertile soils result in poor tree growth. For the black cherry, yellow-poplar, and red maple trees studied, radial tree growth was apparently reduced as a result of the artificial acidification of WS3.

Soil chemistry data proved that WS3 and WS7 were both becoming more infertile by declining Ca concentrations and increasing Al concentrations. WS3 was becoming infertile at a faster rate due to the 12 years of ammonium sulfate treatments that accelerated the effects of acidic deposition. Soil Ca/Al molar ratios provided evidence that WS3 trees were at greater risk of adverse growth effects.

Tree wood chemistry data were more difficult to interpret because of differences between the three tree species. Black cherry and yellow-poplar were obviously affected by the accelerated soil acidification on WS3. Decreases in the Ca/Mn and Mg/Mn molar ratios of black cherry and yellow-poplar bolewood compared to WS7 trees were evident. Red maple trees had similar patterns in Ca/Mn and Mg/Mn ratios, but the treatment vs. control differences were much smaller. It was not possible to determine the exact timing of tree-ring chemical changes in black cherry, yellow-poplar, and red maple trees; consequently, tree wood chemistry was not useful in determining the timing of dendrochemical changes in this case.

Regardless of what the soil and tree chemistry results indicated, tree growth results revealed what was happening to these three tree species when exposed to acidic deposition. Radial tree growth results indicated that black cherry trees on WS3, the treatment watershed, experienced significantly increased growth from four to seven years after treatments began compared to WS7. This was followed by a significant decrease in growth in years nine to eleven. Basal area increment results were similar. Radial tree growth results for yellow-poplar trees on WS3 indicated slight increase (not significant) in growth from year five through seven followed by significantly decreased growth in years nine through twelve when compared to WS7. Yellow-poplar basal area results were similar. Radial growth results for red maple were different in that red maple on WS3 were growing slower than those on WS7 in all years after treatment and significantly slower in years ten through twelve. Interestingly, the basal area results indicated that red maple trees on WS3 were growing better than WS7 trees in all years up until 1993, when the basal area in WS3 suddenly dropped below WS7. The results of this study provide evidence that the long-term treatment of WS3 with ammonium sulfate has accelerated soil acidification to the point where Ca/Al ratios of mineral soil are at stressful levels, which is altering bolewood chemistry and radial growth of the tree species studied has been reduced significantly.

Chapter 5

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APPENDIX

BOLEWOOD CHEMISTRY MOLAR RATIOS

Black Cherry Ca/Mn Molar Ratios

	WS3	WS7
1976-1980	16.43543	17.772798
1981-1985	11.94955	16.77719
1986-1988	12.11806	15.677334
1989-1992	7.253715	13.850312
1993-1996	5.89624	12.535777
1997-2000	5.384058	12.702926

Yellow-Poplar Ca/Mn Molar Ratios

	WS3	WS7
1976-1980	13.9596	28.341872
1981-1985	10.75245	25.336057
1986-1988	8.11449	20.76313
1989-1992	6.820126	19.299495
1993-1996	7.244307	21.52648
1997-2000	7.852863	23.487078

Red Maple Ca/Mn Molar Ratios

	WS3	WS7
1976-1980	5.526746	7.817237
1981-1985	5.37044	7.76936
1986-1988	5.362632	7.670616
1989-1992	5.479807	7.646481
1993-1996	5.631413	7.333593
1997-2000	5.837931	6.863389

Black Cherry Mg/Mn Molar Ratios

	WS3	WS7
1976-1980	2.630818	3.2887728
1981-1985	2.164188	3.2947127
1986-1988	1.971727	2.696672
1989-1992	1.866937	3.3546011
1993-1996	2.244726	3.4512421
1997-2000	2.509396	4.6867828

Yellow-Poplar Mg/Mn Molar Ratios

	WS3	WS7
1976-1980	3.806881	5.4930408
1981-1985	2.879102	5.1204572
1986-1988	2.472407	4.755969
1989-1992	2.473812	4.4249788
1993-1996	2.369968	4.8354554
1997-2000	2.907103	5.7953128

Red Maple Mg/Mn Molar Ratios

	WS3	WS7
1976-1980	1.122007	1.601908
1981-1985	1.070829	1.568274
1986-1988	1.03719	1.534595
1989-1992	1.050751	1.649607
1993-1996	1.139741	1.475151
1997-2000	1.380242	1.560837

BASAL AREA INCREMENT DATA

Average Basal Area Increment

Year	WS3 YP	WS7 YP	WS3 BC	WS7 BC	WS3 RM	WS7 RM
1973	1608.27	1546.75	1572.18	788.98	479.53	428.78
1974	2554.62	1670.09	1888.63	935.79	589.48	517.26
1975	2017.36	2289.71	2062.19	997.15	648.75	467.65
1976	1704.41	1391.13	1613.28	852.97	514.22	221.75
1977	3354.29	2124.06	2538.81	1383.65	757.73	471.25
1978	2558.35	2146.01	2047.26	1719.55	808.61	487.35
1979	1472.62	1158.17	1227.18	1092.09	527.10	278.58
1980	3478.99	1809.93	2892.57	2074.98	1061.56	626.36
1981	3656.54	2708.95	2932.92	2332.84	1188.00	686.21
1982	3743.20	2749.48	3229.36	2209.72	1180.97	883.42
1983	2966.38	2436.53	2897.59	2027.14	1150.09	841.71
1984	1485.57	1239.65	1074.42	1185.91	568.43	386.84
1985	2288.83	2155.56	2922.35	1801.25	1373.03	790.00
1986	3153.79	3538.58	3479.38	1711.45	1369.49	855.81
1987	2463.88	1902.71	2391.75	1272.35	970.37	728.88
1988	726.23	585.36	696.09	529.22	359.86	302.97
1989	2282.48	1957.17	4078.98	2487.93	1294.11	1054.74
1990	3462.57	2502.60	4253.06	2221.55	1374.79	1151.64
1991	2097.72	1543.01	2466.51	1411.01	992.92	830.30
1992	3499.32	2677.65	4680.52	2083.55	1713.98	1398.67
1993	3096.20	2510.22	4470.83	1659.78	1218.17	1162.30
1994	3859.83	2868.63	4737.36	2283.08	1336.82	1593.72
1995	3705.35	2663.10	3691.73	1858.66	1100.32	1295.59
1996	4460.02	4000.60	3726.22	2431.01	1198.64	1443.92
1997	2289.10	4446.83	1899.20	2083.00	962.45	1327.79
1998	2844.88	5431.51	2083.63	2219.14	983.46	1370.57
1999	1276.16	2502.83	1381.47	1772.69	713.60	849.93
2000	1152.24	2105.47	2197.42	1710.31	603.65	924.54

RAW GROWTH DATA

Average Growth for Black Cherry

	WS3	WS7
1987	0.701852869	0.5672541
1988	0.200691317	0.21571439
1989	1.174441873	1.03337414
1990	1.131093272	0.88880813
1991	0.59238582	0.58006907
1992	1.145972946	0.79061946
1993	1.092301222	0.60797458
1994	1.079153938	0.80445794
1995	0.861650337	0.65085932
1996	0.829526007	0.81080192
1997	0.433390531	0.66458227
1998	0.470272398	0.70809246
1999	0.314712114	0.54910301
2000	0.454098474	0.53722036

Average Growth for Yellow-Poplar

	WS3	WS7
1987	0.718687826	0.688604371
1988	0.187358544	0.205976078
1989	0.615825256	0.65505781
1990	0.787504259	0.706513588
1991	0.47635157	0.465236055
1992	0.80437934	0.807432784
1993	0.802778143	0.662751508
1994	0.933857648	0.825268658
1995	0.84635574	0.692982962
1996	0.898978895	1.061774936
1997	0.413895977	1.109705029
1998	0.509382218	1.290645539
1999	0.308876558	0.583435976
2000	0.272313993	0.479952452

Average Growth for Red Maple

	WS3	WS7
1987	0.720948711	0.819382179
1988	0.274495609	0.367006714
1989	0.948504375	1.298651197
1990	0.949929532	1.40390759
1991	0.676815554	0.83493827
1992	1.160162278	1.547758205
1993	0.785313217	1.208331417
1994	0.864247218	1.613444948
1995	0.67519089	1.245130458
1996	0.73864986	1.300828396
1997	0.584381543	1.063207008
1998	0.602476458	1.109186559
1999	0.43844158	0.681594825
2000	0.352402857	0.630730184