

## Chapter 3

# SOIL CHEMICAL RESPONSE TO EXPERIMENTAL ACIDIFICATION TREATMENTS

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## 1. INTRODUCTION

One of the conclusions reached during the Congressionally mandated National Acid Precipitation Program (NAPAP) was that, compared to ozone and other stress factors, the direct effects of acidic deposition on forest health and productivity were likely to be relatively minor. However, the report also concluded “the possibility of long-term (several decades) adverse effects on some soils appears realistic” (Barnard et al. 1990). Possible mechanisms for these long-term effects include: (1) accelerated leaching of base cations from soils and foliage, (2) increased mobilization of aluminum (Al) and other metals such as manganese (Mn), (3) inhibition of soil biological processes, including organic matter decomposition, and (4) increased bioavailability of nitrogen (N).

Sulfate-induced acidification occurs as the sulfate (SO<sub>4</sub>) adsorption potential of a soil is reached, and excess SO<sub>4</sub> ions are leached from the soil into surface and ground waters (Reuss and Johnson 1986). Unlike nitrate (NO<sub>3</sub>), SO<sub>4</sub> is often strongly adsorbed in the soil. Nonetheless, when excess SO<sub>4</sub> appears in percolating soil water, charge balance dictates that a counter ion such as calcium (Ca) must also be present. Consequently, continual leaching of excess SO<sub>4</sub> can gradually decrease exchangeable base cation

pools in the soil if the rate of base cation supply to the soil is not able to keep up with the new equilibrium.

Although  $\text{NO}_3$  is poorly adsorbed in soil systems by abiotic mechanisms, soils represent the largest storage pools for N inputs (Fenn *et al.* 1998), although plant uptake is also important. Nitrogen saturation occurs when the combination of external and internal sources of N exceeds biological demand, resulting in  $\text{NO}_3$  leaching (Ågren and Bosatta 1988, Aber 1992, Stoddard 1994). Other symptoms of N saturation include: increased rates of N cycling, leaching of base cations from the soil, increases in foliar N, and changes in vegetative productivity (Fig. 1-3; Aber 1992, Magill *et al.* 1997, Fenn *et al.* 1998, Lovett *et al.* 2000).

The original study design for the Fernow Acidification Study did not include evaluating impacts on soils, focusing instead on solution chemistry. Soils were fully incorporated into the study beginning in 1994, in an effort to better document changes in ecosystem processes at all levels. Results from sampling for the Direct Delayed Response Program suggested that the soils on the Fernow watersheds were relatively low in  $\text{SO}_4$  adsorption capacity, that effects of the additions of ammonium sulfate fertilizer would manifest fairly rapidly, and would most likely be an acidification response to sulfur (S) (Herlihy *et al.* 1993). However, N appeared to be as important as S in defining acidification processes, based on early stream chemistry responses. Therefore, a number of studies evaluating N cycling processes in the soil also were conducted, and will be discussed in this chapter. We will present information on soil chemistry for WS3, WS4, WS7 and WS9 (Table 3-1, See Chapter 2 for more detailed watershed descriptions.), and will focus on those chemical constituents believed to be most sensitive to acidification or N saturation: pH, N, Ca, magnesium (Mg), Al and Mn. Other data will be included as needed for supporting arguments.

## **2. METHODS**

### **2.1 Comparisons between WS3 and WS4**

In 1988, as the study was being planned, 15 sites per watershed on WS3 and WS4 were selected for the measurement of soil solution by lysimetry (Fig. 3-1). WS3 serves as the treatment watershed and WS4 is the reference watershed. (See Chapter 2 for detailed descriptions of the watersheds.) At each site, prior to lysimeter installation, a soil pit was excavated and the major horizons were described. Mineral soil samples were collected from each pit and each horizon for analysis; the forest floor was not sampled. Unfortunately, most of these soil samples and the associated chemical and

physical data were lost. The few archived soil samples that were retained were analyzed in 1994 for chemical properties at the University of Maine Plant and Soil Testing Laboratory, using analytical methods described below. These data will be used to provide insights on pretreatment conditions, and to evaluate changes over time.

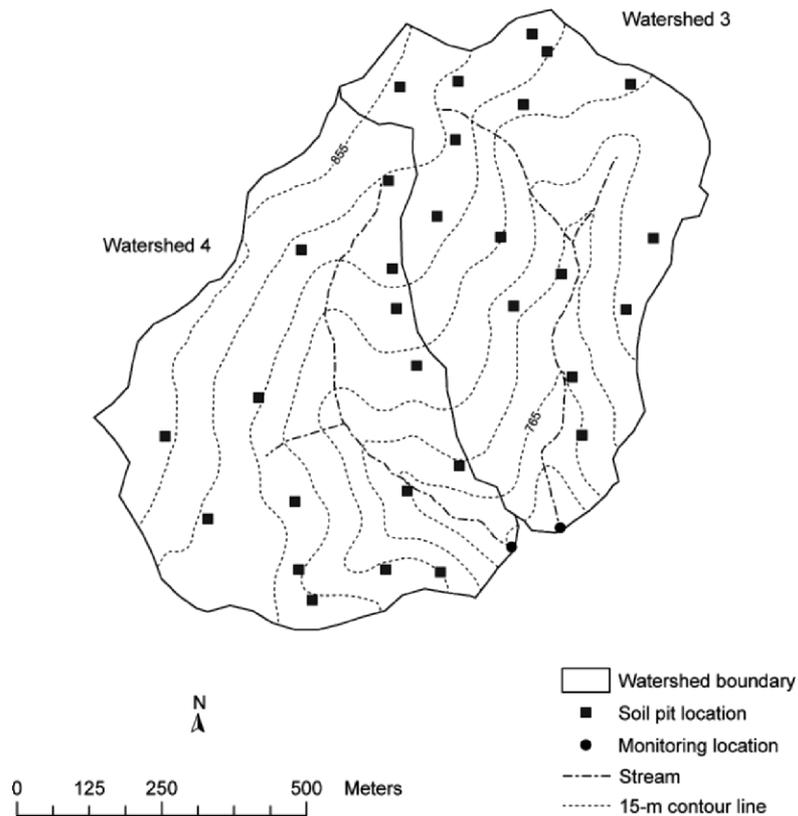


Figure 3-1. WS3 and WS4 soil pit locations.

These 15 lysimeter sites per watershed were resampled in adjacent, undisturbed soil in 1994 and 2002. On each of these sampling dates, soil samples were collected a short distance away from the lysimeters, along the contour (e.g. at the same elevation and aspect). Samples were collected from the O horizon (Oa and Oe horizons were not separated), and the mineral soil by depth (0-10, 10-20, 20-30 and 30-45 cm), which approximately correspond to the A, AB, BW1 and BW2 horizons as described in 1988.

Samples were air-dried, sieved (2 mm) and analyzed for chemical constituents. Soil pH was measured in distilled water (1:1 ratio). Organic matter concentration was estimated by loss-on-ignition (LOI) at 550°C (Page *et al.* 1982). Total N was measured by the macro Kjeldahl method in 1994 and by combustion in 2002. The two methods give comparable results in these types of soils (Bruce Hoskins, Univ. Maine Soil Testing Laboratory, pers. comm., 1998). All other nutrients were extracted with 1N ammonium chloride and measured by plasma emission, or in the case of potassium (K) and sodium (Na), by flame emission. Exchangeable acidity was extracted by 1N potassium chloride and measured by titration (Page *et al.* 1982). Base saturation was calculated as the percentage of the effective cation exchange capacity (ECEC) occupied by exchangeable bases, whereas Ca or Mg saturation was the percentage of the ECEC occupied by these individual exchangeable cations.

Data were analyzed using “Proc Mixed” (SAS Institute, Inc. 1988) with a restricted maximum likelihood estimation technique. Year was a repeated variable in the analysis and was modeled using an autoregressive order 1 covariance structure. Data were log-transformed to meet the assumptions of normality and equality of variances. Base saturation and LOI data were transformed using the arcsine transformation, which is more appropriate for percentage data. Note that for soil Ca, no transformations were successful in meeting the assumptions of normality and equality of variances and therefore results should be interpreted with extreme caution. Other watersheds were sampled for related studies; those data are included here for comparative purposes.

## **2.2 Comparisons between WS3 and WS7**

Two sets of soil samples were collected during the acidification experiments that allowed comparison of soil conditions on WS3 and WS7. For these comparisons, WS7 serves as the vegetative reference for the treated WS3. See Chapter 2 for details on the watersheds’ characteristics. Tepp (1995) sampled soil in the vicinity of 25 randomly located litter collectors on WS3 and WS7 in May 1995, after approximately 7 years of ammonium sulfate treatments. Tepp collected samples from soil A horizons (mean depths 5.9 and 7 cm on WS3 and WS7, respectively) and soil B horizons (mean depths 18.6 cm and 22.1 cm for WS3 and WS7, respectively) within 2 m of the litter collectors (Fig. 3-2). Soil samples were analyzed for available phosphorus (P), K, Ca, and Mg using the Mehlich 3 method (Wolf and Beegle 1991) at The Pennsylvania State University Agricultural Analytical Services Laboratory. Available metals (Mn, iron (Fe), copper (Cu), zinc (Zn), Na, Al, lead (Pb), nickel (Ni), cadmium (Cd)) were analyzed at the same

facility using the Diagnostic Soil Test Methods (ASTM D5435-93) and pH using the water method (Eckert and Sims 1991). Odenwald (2002) sampled soil O, A, and B horizons in the vicinity of 10 trees sampled for growth cores and dendrochemistry on WS3 and WS7 in 2000. (See Chapter 5 for further details), 12 years after the initiation of treatments. These samples were also analyzed for soil chemical parameters at the Penn State Agricultural Analytical Services Laboratory using methods described above. In addition, a strontium chloride ( $\text{SrCl}_2$ ) extraction aluminum stress test analysis was used to determine plant available Ca and Al at The Pennsylvania State University Agricultural Analytical Services Laboratory (Odenwald 2002).

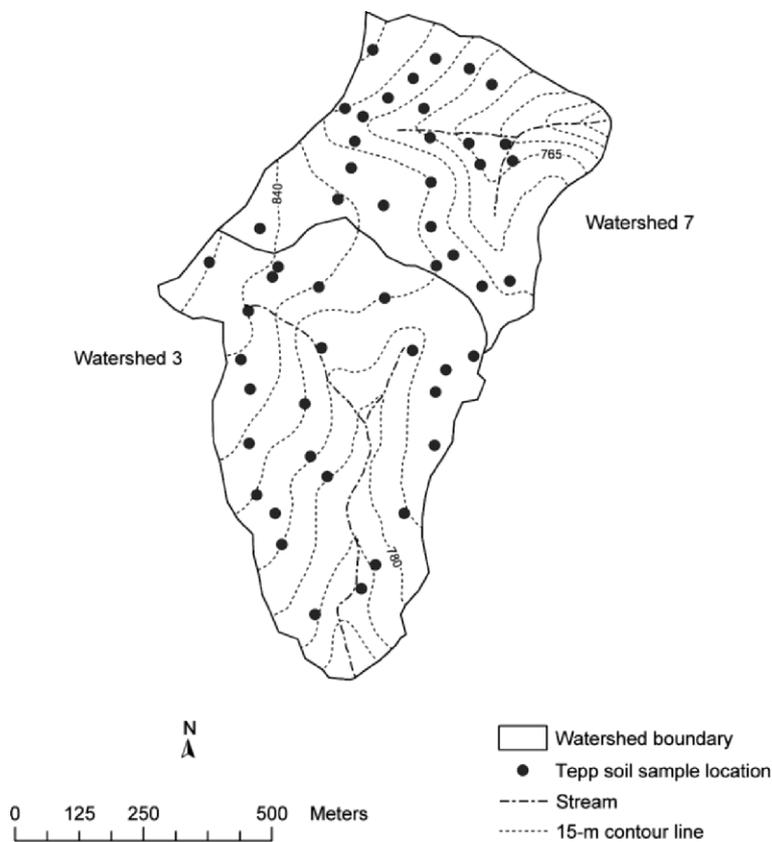


Figure 3-2. Tepp (1995) soil sampling locations.

### 2.3 Effects on Soils on WS9

Each year from 1992-1994, soil samples were collected from one control plot and one treatment plot (Fig. 3-3) in July (prior to the July fertilizer application) and in August (post-fertilization). In 1992, six control and six treated soil pits (approximately 20 x 20 cm) were excavated in each plot. In 1993 and 1994, 12 pits on each plot were hand excavated and soil samples were obtained from each. All soil samples were collected from the 0-2 cm layer (O horizon) and the 2-10 cm layer (A horizon). These horizons were chosen to represent the effective rooting horizons for this soil (Kochenderfer

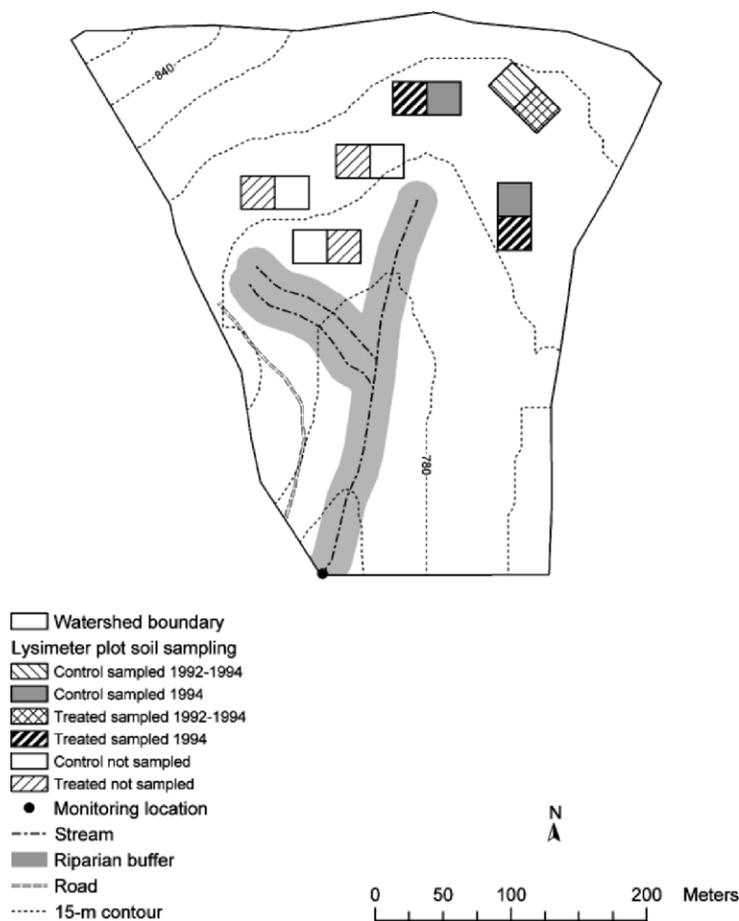


Figure 3-3. Soil sampling locations on WS9.

1973). All analyses were conducted on air-dried soil sieved to 2 mm, at the Environmental Resources Research Institute Soil Chemistry Laboratory at The Pennsylvania State University. Soil pH was determined in water with soil-to-solution ratios of 1:1 for both soil horizons (Black 1964). The base cations, Ca, Mg, and K, and metal cations Al and Mn were determined by atomic absorption spectrophotometry following 0.01 M SrCl<sub>2</sub> extraction and preparation as outlined by Joslin and Wolfe (1989). In 1992, soil carbon (Schulte 1991), NO<sub>3</sub>-N (Isaac and Johnson 1976) and SO<sub>4</sub>-S (Black 1964) analyses were performed by the Agricultural Analytical Laboratory at The Pennsylvania State University. In 1993 and 1994, total carbon (C) and total N were analyzed by combustion using an elemental analyzer and total S by combustion using an elemental analyzer with an electron capture detector (Baccanti et al. 1993, Carlo Erba Instruments 1990) at the USDA Forest Service's Timber and Watershed Laboratory in Parsons, West Virginia.

Statistical analysis followed a Model I two-treatment ANOVA for a fixed treatment, incorporating t-tests for means comparisons (SAS Institute 1988). All significant differences are reported at  $p \leq 0.05$ .

### 3. RESULTS

#### 3.1 Pretreatment Soil Characteristics – WS3, WS4, WS7

A rock layer composed of fractured hard sandstone and shale underlies most of the Fernow watersheds. Slopes ranging from 20 to 50 percent are common. The soils are predominantly from the Calvin and Dekalb soil series, which originated from these rocky materials (loamy-skeletal mixed mesic Typic Dystrochrepts). The Calvin series consists of moderately deep, well-drained soils formed in material weathered from interbedded shale, siltstone and sandstone. Dekalb soils are also acidic, deriving from acidic sandstones. Average soil depth is about 1 m, and the soil contains a considerable amount of stones and large gravels, as much as 70% by volume (Adams et al. 2004). Average bulk density of the whole soil ranges from 1.2 to 1.5 g cm<sup>-3</sup>, with average porosity 43 to 55% (Adams et al. 2004).

From the relatively few pretreatment samples, we may conclude that there were few pretreatment differences (1988) between the upper mineral horizon (0-10 cm) on WS3 and WS4 (Table 3-1). Edwards et al. (2002a) reported that WS3 had a significantly greater A horizon (approximately 0-10 cm) soil pH than WS4, and significantly lower exchangeable Al than WS4, but noted no other statistically significant differences in the upper horizon chemistry. Base saturation of the A horizon soil on WS3 was more than twice that of WS4 A horizon, and indeed, almost twice that of the other

watersheds, but the differences were not statistically significant (Table 3-1). Some of this is due to very high Ca values within one location on WS3, and thus is attributed to high spatial variability. Within-watershed variability was large and the number of samples was fairly small.

The soils of all watersheds were fairly acidic, with moderately low ECEC and base saturation. Based on work by Reuss (1983), these soils are at the thresholds where an abrupt change from Ca to Al mobilization should occur with acidification. Overall, the variability in soil chemical properties among watersheds was not great. The watersheds designated to be treated, WS3 and WS9, had the highest base saturation levels, suggesting a relationship with stand age perhaps. However, mean base saturation on WS7, also a young stand, was the lowest (Table 3-1). Gilliam and Adams (1995) evaluated the relationship between soil chemical properties and stand age for these watersheds, but found no statistically significant relationship. However, exchangeable nutrients were more highly correlated with organic matter content and texture in the young stands than in the mature stands that they studied, which the authors interpreted to mean that the importance of soil organic matter as a source of nutrients or cation exchange sites might decrease with stand age.

*Table 3-1.* Soil chemistry means and standard deviations (in parentheses) for Fernow watersheds for upper mineral soil horizon (0–10 cm on average), selected parameters. Data for WS3 and WS4 are mean pretreatment soil levels ( $n = 12$  and  $n = 6$ , respectively). Data for other watersheds represent different sampling dates. NA= data not available.

Analyte	Watershed, stand origination date, and treatment				
	WS3 1969 Fertilization	WS4 ~1911 Reference	WS7 <sup>a</sup> 1969 Vegetative Reference	WS10 <sup>b</sup> ~1911 Reference	WS9 <sup>c</sup> 1984 Fertilization
pH	4.48	3.95	4.68	3.96	4.56
Total C (g kg <sup>-1</sup> )	91 (54)	112 (53)	NA	62 (23)	33 (13)
Total N (g kg <sup>-1</sup> )	4.79 (1.38)	2.6 (1.4)	4.5 (1.3)	3.1 (0.8)	NA
Exch. Ca (meq 100g <sup>-1</sup> )	4.79 (8.72)	0.49 (0.22)	1.28 (1.82)	0.5 (0.3)	0.64 (0.57)
Exch. Mg (meq 100g <sup>-1</sup> )	0.59 (0.88)	0.23 (0.10)	0.28 (0.20)	0.22 (0.08)	0.17 (0.12)
Exch. Al (meq 100g <sup>-1</sup> )	1.39 (1.81)	8.70 (3.79)	1.88 (0.53)	0.50 (0.03)	4.23 (0.85)
Base saturation (%)	34 (33)	14 (4)	13 (14)	14 (7)	21 (12)
ECEC (meq 100g <sup>-1</sup> )	11.77 (7.86)	9.35 (3.41)	14.6 (1.83)	8.50 (2.1)	6.50 (1.0)

<sup>a</sup> Data from Tepp (1995).

<sup>b</sup> Note that 0-10 cm in WS10 includes Oe and Oa horizons, where present, but not in WS3 and WS4. WS10 was sampled in 1997 (Christ *et al.* 2002).

<sup>c</sup> Data from Edwards *et al.* (2002b).

Helvey and Kunkle (1986) demonstrated that much more  $\text{SO}_4$  entered WS4 as throughfall than was lost in streamflow on an annual basis, suggesting net watershed accumulation, and significant  $\text{SO}_4$  buffering capacity by the soil. However, Polk (1991) examined Berks and Dekalb soils from Fork Mountain and concluded that the soils had little further ability to absorb  $\text{SO}_4$ . Helvey and Kunkle (1986) also demonstrated that  $\text{NO}_3\text{-N}$  inputs were approximately equal to outputs. Nitrate was generally the dominant form of available N on both watersheds (Gilliam and Turrill 1993).

### **3.2 Pretreatment Soil Characteristics – WS9**

The predominant soil on WS9 is Calvin channery silt loam (loamy-skeletal, mixed mesic Typic Dystrochrept), similar to that of WS3, WS4, and WS7. However, WS9 was farmed for many years before 1930 (Lima et al. 1978), and soils on the watersheds were nutrient-poor even 50 years later (Table 3-1), with relatively high exchangeable Al levels, and the lowest exchangeable Mg and ECEC of the watersheds evaluated. Much of the original A horizon soil has been eroded from the slopes of WS9 (Kochenderfer and Helvey 1989).

### **3.3 Treatment Effects**

#### **3.3.1 Comparisons between WS3 and WS4**

The effect of Horizon was statistically significant for all the variables, as might be expected. There is an order of magnitude difference in soil carbon, for example, between the O horizon and the 30-45 cm horizon. The differences among horizons were largely driven by higher concentrations and nutrient values in the O horizon, due to the greater organic matter content. The 0-10 cm horizon usually differed significantly from the O horizon and from the deeper horizons, and there were few significant differences among the lower horizons (10-20, 20-30 and 30-45 cm horizons). This trend of decreasing nutrient concentrations and organic matter with depth is common in these soils, and points to the importance of annual litter inputs in nutrient cycling, and to the role of uptake by vegetation.

Year was a statistically significant effect for all variables except for acidity and Mg, although lack of data for the O horizon in 1988, and the relative paucity of data for 1988 in general, made interpretation of these data difficult. The horizon\*year interaction was statistically significant for all variables, again due to the influence of the O horizon, and in particular, changes in O horizon nutrient concentrations between 1994 and 2002 (Tables 3-2 and 3-3). Total carbon, total N, pH base saturation, Ca saturation, ECEC,

and K all increased significantly in the O horizon between 1994 and 2002. The lowest horizons showed little (20-30 cm) or no change (30-45 cm) over time.

*Table 3-2.* Chemical characteristics of soils on WS3 and WS4, 1994. Values are means of 15 samples; values within an horizon followed by different letters indicate significant differences between watersheds at  $p < 0.05$ .

Characteristic	Depth (cm)									
	O horizon		0-10		10-20		20-30		30-45	
	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4
pH	4.22	4.07	4.34	4.34	4.57	4.55	4.55	4.51	4.50	4.54
Total C (g kg <sup>-1</sup> )	108	189	57	53	28	26	20	17	9	7
Total N (g kg <sup>-1</sup> )	5.97a	8.75b	3.84	3.11	1.68	1.25	1.07	0.72	0.91	0.54
C:N	18.1	20.4	15.6	18.0	18.3	22.1	22.0	24.6	10.8	15.4
Ca (meq 100g <sup>-1</sup> )	3.32	4.56	1.55	0.48	0.32	0.14	0.32	0.11	0.36	0.12
K (meq 100g <sup>-1</sup> )	0.39	0.74	0.26	0.20	0.14	0.12	0.14	0.11	0.14	0.12
Mg (meq 100g <sup>-1</sup> )	0.63	1.07	0.33	0.22	0.11	0.09	0.09	0.08	0.09	0.08
Na (meq 100g <sup>-1</sup> )	0.08	0.11	0.06	0.04	0.03	0.04	0.03	0.03	0.03	0.03
Base saturation (%)	29.6	40.9	20.1	12.8	11.7	7.8	12.0	7.1	11.1	7.5
Ca saturation (%)	21.4	28.9	13.4	6.5	6.2	2.8	6.8	2.5	6.3	2.6
Mg saturation (%)	4.6	6.7	3.3	2.9	2.1	1.8	1.9	1.6	1.8	1.7
Exch. acidity (meq 100g <sup>-1</sup> )	8.4	9.2	7.2	6.7	4.6	4.9	4.5	4.6	4.8	4.8
ECEC (meq 100g <sup>-1</sup> )	12.9	15.7	9.4	7.6	5.3	5.3	5.1	4.9	5.4	5.1

The Watershed effect was statistically significant only for Ca and ECEC, suggesting that the treatments may have altered Ca throughout the soil profile, and therefore ECEC. Generally, WS3 mean Ca and ECEC values were greater than for WS4. However, because of the variability of these data, and because the Ca data did not meet the assumptions of normality and equality of variances, this conclusion cannot be made with confidence. A significant watershed\*horizon effect was detected only for K and total C. Significant watershed\*year effect was detected for acidity, Mg, and Ca

saturation. The watershed\*horizon\*year effect was statistically significant only for pH, total N, Mg, K, and total C.

Table 3-3. Chemical characteristics of soils on WS3 and WS4, 2002. Values are means of 15 samples; values within an horizon followed by different letters indicate significant differences between watersheds at  $p < 0.05$ .

Characteristic	Depth (cm)									
	O horizon		0-10		10-20		20-30		30-45	
	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4
pH	4.10	4.14	4.20	4.13	4.61	4.54	4.74	4.71	4.78	4.72
Total C (g kg <sup>-1</sup> )	268	249	73	60	40	37	18	18	9	8
Total N (g kg <sup>-1</sup> )	13.84	10.38	4.35	3.61	2.45	2.37	1.22	1.20	0.71	0.69
C:N	19.4	23.8	15.4	15.7	14.5	16.8	20.8	18.1	13.0	11.6
Ca (meq 100g <sup>-1</sup> )	11.93	12.86	1.47	0.83	0.46	0.29	0.19	0.17	0.21	0.11
K (meq 100g <sup>-1</sup> )	1.11	1.13	0.30	0.34	0.22	0.19	0.14	0.15	0.12	0.10
Mg (meq 100g <sup>-1</sup> )	1.85	1.93	0.24	0.24	0.10	0.12	0.05	0.09	0.05	0.05
Na (meq 100g <sup>-1</sup> )	0.08	0.07	0.01	0.06	0.01	0.02	0.01	0.02	0.01	0.01
Base saturation (%)	61.1	67.0	19.9	22.8	12.6	11.6	8.1	9.5	7.4	5.4
Ca saturation (%)	48.3	53.7	13.6	13.6	7.1	5.7	4.0	3.9	4.1	2.2
Mg saturation (%)	7.7	8.2	3.5	5.1	3.7	3.4	2.8	3.2	2.2	1.9
Exch. acidity (meq 100g <sup>-1</sup> )	8.3	7.3	7.0	5.9	5.6	5.1	4.8	4.2	5.4	4.8
ECEC (meq 100g <sup>-1</sup> )	23.4	23.3	9.1	7.3	6.4	5.7	5.2	4.6	5.8	5.1

Thus, we may conclude that there are significant differences in most chemical parameters among the upper two horizons (O and 0-10 cm), and the mean values of some chemical variables changed over time. In general, the differences among watersheds were not statistically significant, and did not provide strong evidence of decreases in base cation concentrations. The O horizon showed significant changes between 1994 and 2002, particularly related to changes in organic matter content. During this time period, organic matter increased more on WS3 (150%) than on WS4 (32%), although initial C levels were greater on WS4. The increase in total N also was greater on

WS3 (125%) relative to the changes on WS4 (20%), resulting in lower C:N ratios on WS3 than WS4 in 2002 (Fig. 3-4).

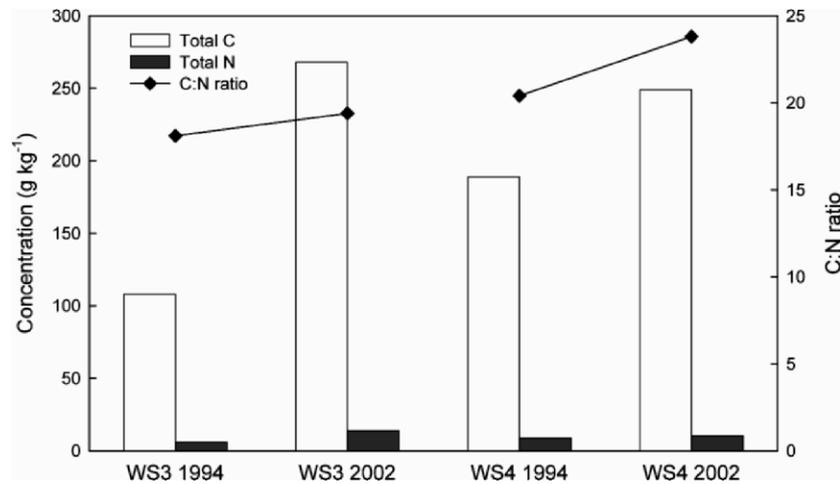


Figure 3-4. Total soil C, total soil N and C:N ratios for O horizon, WS3 and WS4, sampled in 1994 and 2002.

ECEC also increased significantly in the O horizon for both watersheds, but exchangeable acidity did not (Fig. 3-5). In addition, WS3 O horizon concentrations of Ca, K, and Mg, all increased significantly between 1994 and 2002, perhaps reflecting increased uptake of nutrients by the vegetation and storage in leaves, and eventually increased concentrations in leaf litter. Fertilizer additions also may have increased litter mass and organic matter delivery to the soil surface, although litterfall data do not show increases in litterfall mass on WS3 over time. Higher quality litter (that with more soluble N, more easily decomposed) would mineralize more quickly, which could result in more organic matter but in a more mature state of humification with higher surface charge.

There were fewer statistically significant differences in the O horizon between the two watersheds in 2002 relative to 1994, suggesting the O horizons of the two watersheds may be becoming more similar with time and perhaps treatment. Gilliam *et al.* (2001a) concluded that the acidification treatment appeared to decrease the spatial and temporal variability of some soil properties within WS3, particularly those related to N cycling. Decreased spatial heterogeneity within a watershed might lead to greater ability to detect differences between watersheds.

Based on these data, the O horizon appears to be the most sensitive to change over time, as statistically significant changes in most nutrient

concentrations, generally increases, were observed for both watersheds between 1994 and 2002. The O horizon showed the most changes over time probably because of differences in total C, and given the reactivity of organic matter in these soils it is reasonable to expect that many other things would also change in concert with organic matter. A similar responsiveness in the O horizon was reported for the Bear Brook Watershed Manipulation study in Maine (Fernandez et al. 2003).

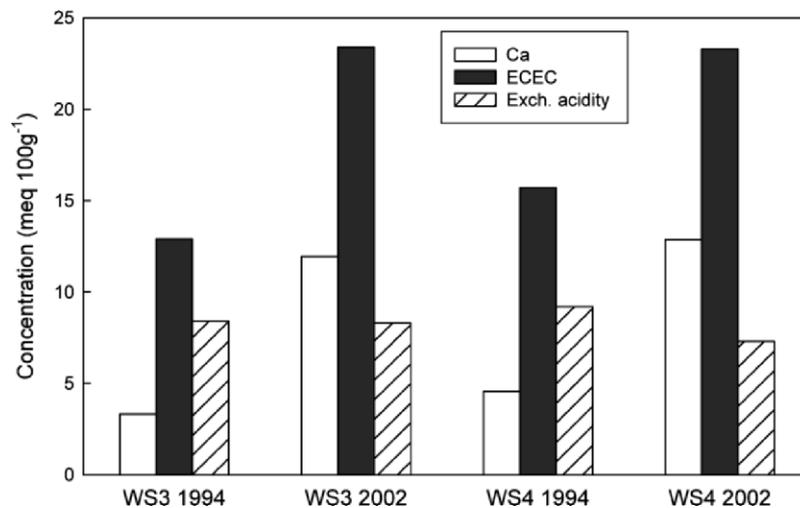


Figure 3-5. Exchangeable soil Ca, ECEC and exchangeable soil acidity for O horizon, WS3 and WS4, sampled in 1994 and 2002.

To further extend these temporal trends, and allow some evaluation of possible treatment effects on soil chemistry, we evaluated changes in average values for a number of soil parameters for the locations sampled in each of 1988, 1994 and 2002 (four pits in WS3 and three in WS4). We focus on the 0-10 cm and 10-20 cm horizons for clarity of presentation (Figs. 3-6 through 3-10), and because the changes in the lower horizons were subtle to nonexistent. There is a trend of increasing mean organic matter content, as measured by LOI, over the 14-year period, on both watersheds, with the exception of the 0-10 cm horizon of WS4 (Fig. 3-6) where organic matter content is decreasing slightly over time. Calcium and Mg concentrations generally declined over time in the upper mineral horizons of both watersheds (Figs. 3-7 and 3-8, respectively), although there were slight increases in the mean Ca concentration between 1994 and 2002 in the 0-10 cm of WS3. The greatest changes in mean values occurred between 1988 and 1994, in the upper 10 cm of soil. Variability in Ca and Mg

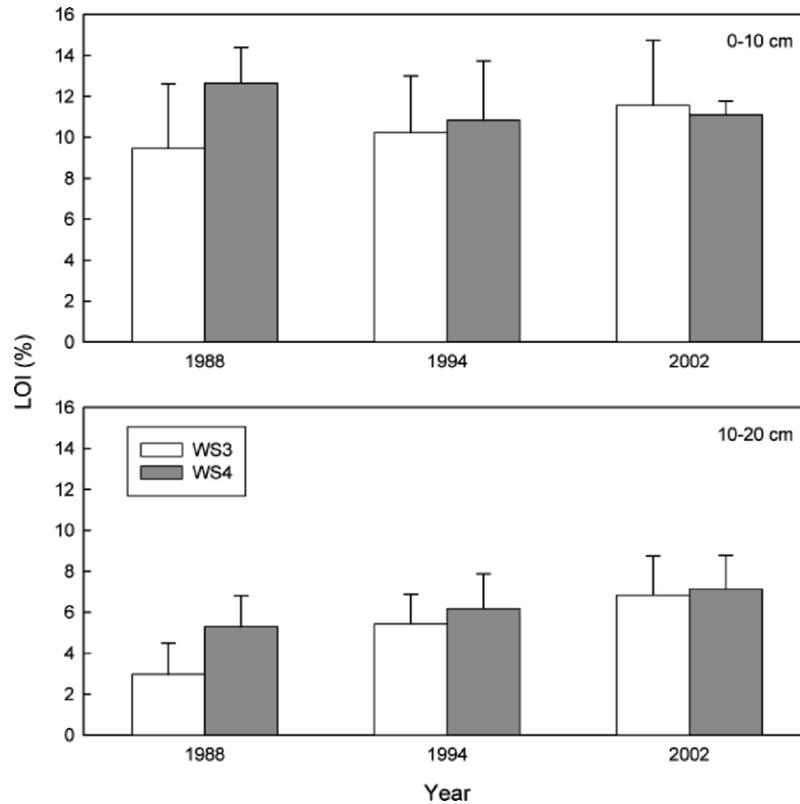


Figure 3-6. Changes in LOI over time, WS3 and WS4.

concentrations was also quite large in the 0-10 cm horizon for the 1988 sampling in particular. ECEC decreased for both watersheds, although most consistently in WS3 (Fig. 3-9). Base saturation increased over time for WS4 while decreasing on WS3 (data not shown), while exchangeable acidity showed the reverse pattern, increasing in WS3 0-10 and 10-20 cm horizons, and decreasing in WS4 (Fig. 3-10). Note that Ca concentration values from a single location in WS3 (1988) are quite high and are strongly influencing the means and variability. This represents the significant spatial variability discussed earlier. Overall, however, these data suggest a trend on WS3 of increasing acidity and organic matter over time, and decreases in base cations and ECEC, mostly in the upper mineral horizon. Although the data available to examine changes through time are very limited, the general patterns seem to suggest that more change occurred on WS3 between 1988

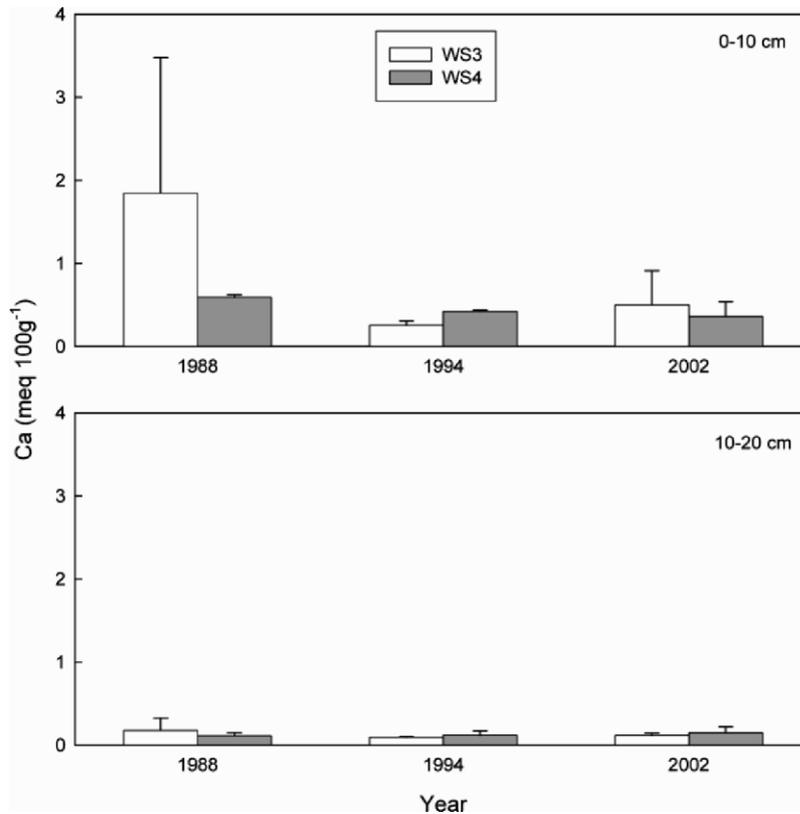


Figure 3-7. Changes in exchangeable soil Ca with time, WS3 and WS4.

and 1994 than between 1994 and 2002. In addition, the direction of the apparent change is what might be expected if soil acidification is occurring, supporting the hypothesis that the treatments are affecting soil processes. The trend of increasing nitrogen in the organic horizon (Tables 3-2 and 3-3) also provides evidence for a treatment effect, as we would expect soil N to increase as a result of chronic N fertilization. However, the effects are difficult to detect with existing data sets. The apparent trends of increasing organic matter in the O horizon (Fig. 3-4), and in the upper mineral soil (Fig. 3-6) of WS3 are intriguing and worthy of further examination and sampling, as organic matter is undoubtedly an important source of nutrients in these soils.

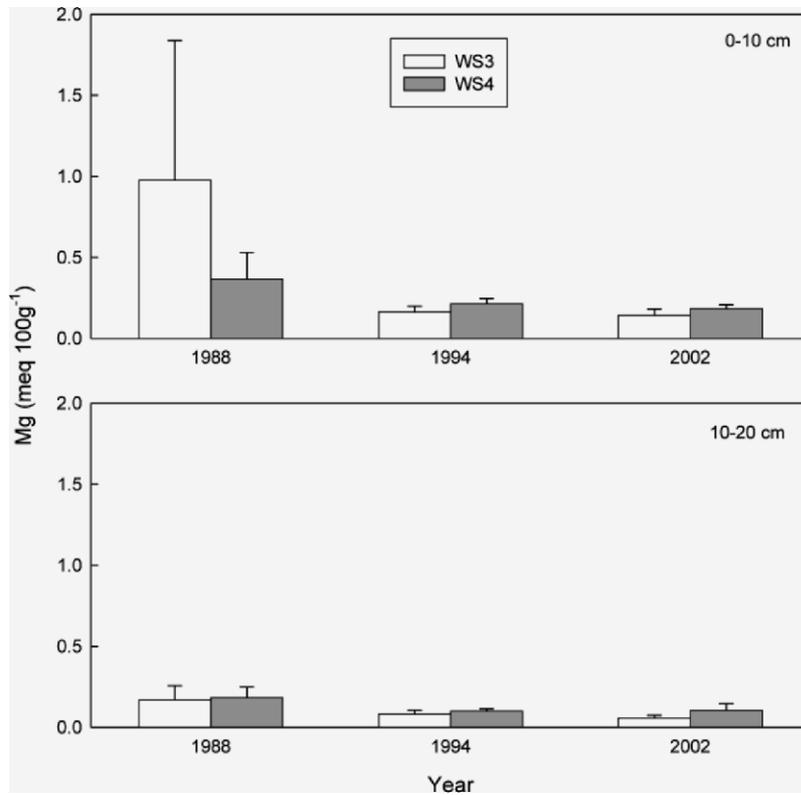


Figure 3-8. Changes in soil Mg over time, WS3 and WS4.

### 3.3.2 Comparisons between WS3 and WS7

Soil on the treated WS3 had lower soil pH and exchangeable base cation concentrations and higher Al concentration than the vegetative reference WS7, after both 7 and 12 years of treatment (Figs. 3-11 through 3-13), although not all differences were statistically significant. Differences in soil pH and A horizon Ca concentrations between the two watersheds were statistically significant in both studies, while Mg and Al levels did not differ significantly in the Tepp (1995) study (Figs. 3-11 and 3-12). Odenwald's (2002) study showed significantly higher Al levels in the soil of WS3. Ca/Al ratios in A and B horizons on the treated basin were at or below unity (Fig. 3-13), a level below which some trees may experience growth stress (Cronan and Grigal 1995).

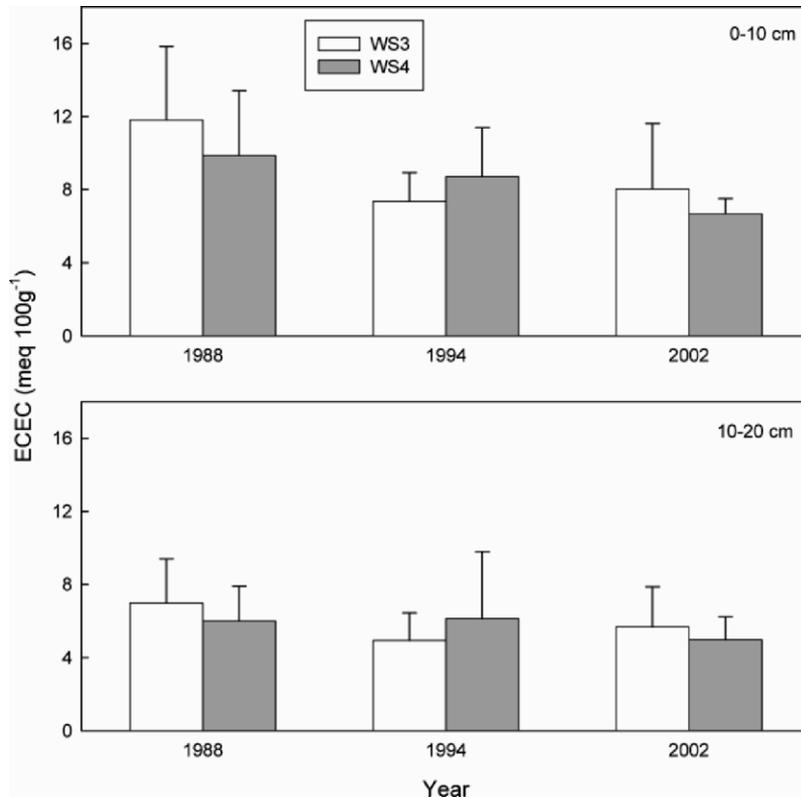


Figure 3-9. Changes in ECEC over time, WS3 and WS4.

Levels of Mn in soil differed between WS3 and WS7 (Tepp 1995), with mean Mn concentrations significantly less on WS3 relative to WS7 after 7 years of treatment. Soil Mn concentrations on the treated watershed in A horizon samples were lower ( $142.6 \text{ mg kg}^{-1}$  on WS3 compared to  $174.0 \text{ mg kg}^{-1}$  on WS7), although not significantly so, but B horizon samples showed significantly lower levels of Mn on the treated basin ( $31.6 \text{ mg kg}^{-1}$  on WS3 compared to  $48.7 \text{ mg kg}^{-1}$  on WS7; Tepp 1995). This was somewhat surprising, as soil acidification was expected to eventually increase Mn availability. On the treated watershed, vegetation also showed lower concentrations in bolewood Mn concentrations after 4 years of treatment in two of four species, but after 8 years of treatment all four tree species showed a higher Mn and lower Ca and Mg in bolewood samples (see Chapter 5). Thus, mineral soil Mn levels were lower 7 years after treatment, while

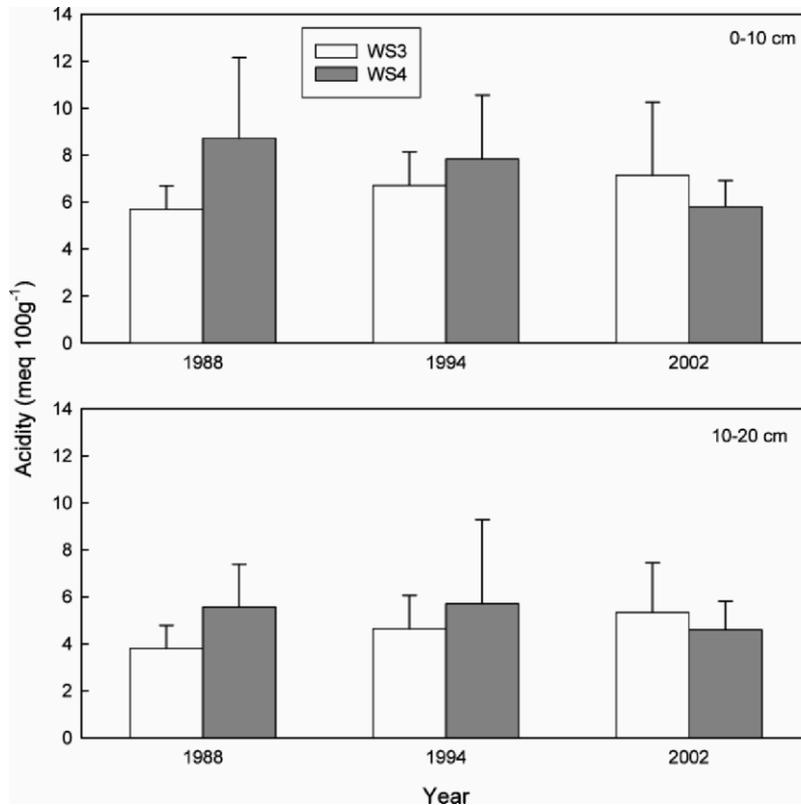


Figure 3-10. Changes in exchangeable soil acidity over time, WS3 and WS4.

vegetation bolewood Mn levels were elevated after 8 years of treatment. These results presumably reflect some complex combination of soil depletion and increased availability due to mobilization, playing itself out in the soil over time and depth.

### 3.3.3 Treatment Effects WS9

Soil on the treated plots sampled in August 1992 had significantly greater N and C concentrations compared to soil from the control plots; for the A horizon these differences were statistically significant. Soil from the A horizon on the treated plots also showed significantly greater SO<sub>4</sub>-S concentrations than those of the control plots. The 1993 July total S concentration in the A horizon was significantly greater than the control. In

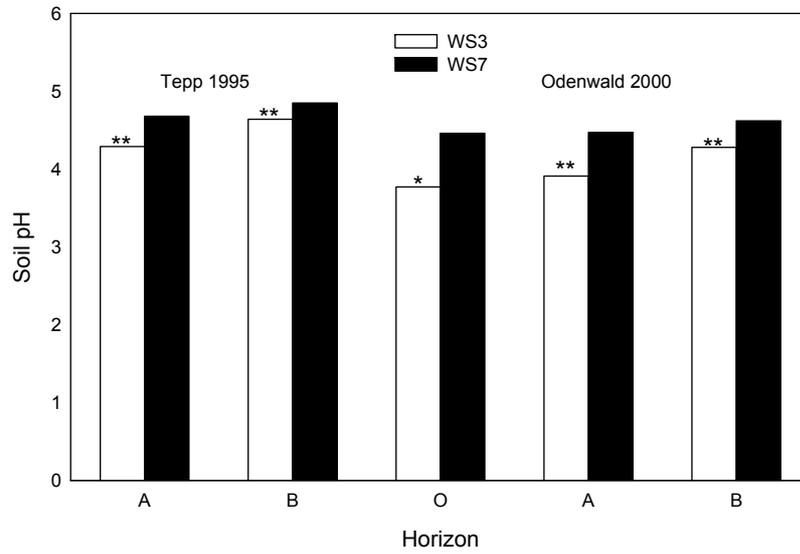


Figure 3-11. Comparisons of soil pH between Fernow WS3 and WS7 by soil horizon after 7 years of treatment (Tepp 1995) and 12 years of treatment (Odenwald 2002). Significant differences are indicated above bars; \* 0.05 level, \*\* 0.01 level.

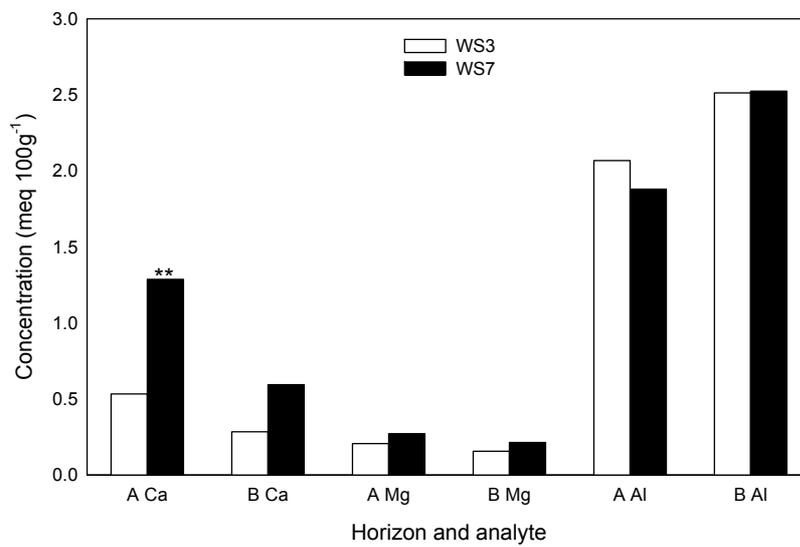


Figure 3-12. Comparison of soil exchangeable Ca, Mg, and Al on Fernow WS3 and WS7 after 7 years of treatment by horizon (Tepp 1995). Significant differences are indicated above bars; \* 0.05 level, \*\* 0.01 level.

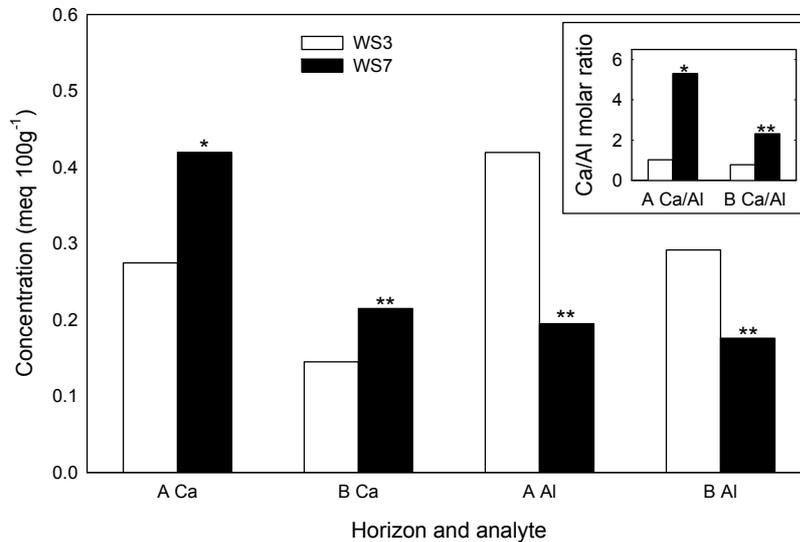


Figure 3-13. Comparison of soil exchangeable Ca and Al and Ca/Al molar ratios on Fernow WS3 and WS7 after 12 years of treatment by horizon (Odenwald 2002). Significant differences are indicated above bars; \* 0.05 level, \*\* 0.01 level.

August 1994, O horizon concentrations of C and N were significantly greater in the treated plots compared to the control plots.

Base cation concentrations also varied between the treatment and control plots in WS9. In 1992, the O horizon Ca concentration was significantly greater in the control plots compared to soil in the treated plots both in July and August (Table 3-4). For the same year, values of SrCl<sub>2</sub> extractable Al in August were significantly greater, and Ca and Mg significantly lower compared to the control, for both horizons. In 1993, SrCl<sub>2</sub> extractable soil Al and Mn were significantly greater in the treated soil compared to the control, for both horizons, and Ca, Mg, and pH were significantly greater in the control plots compared to treated plots, for both horizons (Table 3-4).

In 1994, significant differences between soil from the treated plots and the control plots were found (Table 3-4), and these changes were also evident in the soils sampled from other areas on the watershed (data not shown). The soil pH was significantly greater in the control compared to the treated soil, except for the July A horizon data. Soil Al concentrations were significantly greater in all treated soil samples collected in 1994 compared to controls. Calcium and Mg concentrations were greater in the control plots compared to treated plots (Table 3-4) while soil Mn concentrations were greater in the treated plots (Fig. 3-14). Most differences were significantly different.

Table 3-4. Soil chemistry (0.01 M SrCl<sub>2</sub> extractable) mean concentrations, from control and treated plots (Pickens 1995). Different letters within columns by months indicate statistically significant difference at  $p \leq 0.05$ ;  $n = 6$ .

Date and plot	O Horizon			A Horizon		
	Al	Ca	Mg	Al	Ca	Mg
1992 July	meq 100g <sup>-1</sup>					
Control	0.018a	0.879a	0.119a	0.032a	0.522a	0.058a
Treated	0.033b	0.642b	0.084b	0.081b	0.487b	0.046b
1992 August						
Control	0.029a	0.876a	0.185a	0.022a	0.852a	0.101a
Treated	0.069b	0.519b	0.084b	0.191b	0.154b	0.033b
1993 July						
Control	0.047a	0.794a	0.144a	0.091a	0.555a	0.054a
Treated	0.212b	0.500b	0.096b	0.247b	0.296b	0.029b
1993 August						
Control	0.046a	0.802a	0.149a	0.017a	0.661a	0.069a
Treated	0.136b	0.782b	0.084b	0.188b	0.326b	0.030b
1994 July						
Control	0.010a	0.446a	0.155a	0.076a	0.430a	0.078a
Treated	0.205b	0.423b	0.066b	0.275b	0.303b	0.041b
1994 August						
Control	0.012a	0.539a	0.152a	0.015a	0.635a	0.066a
Treated	0.142b	0.443b	0.072b	0.255b	0.338b	0.028b

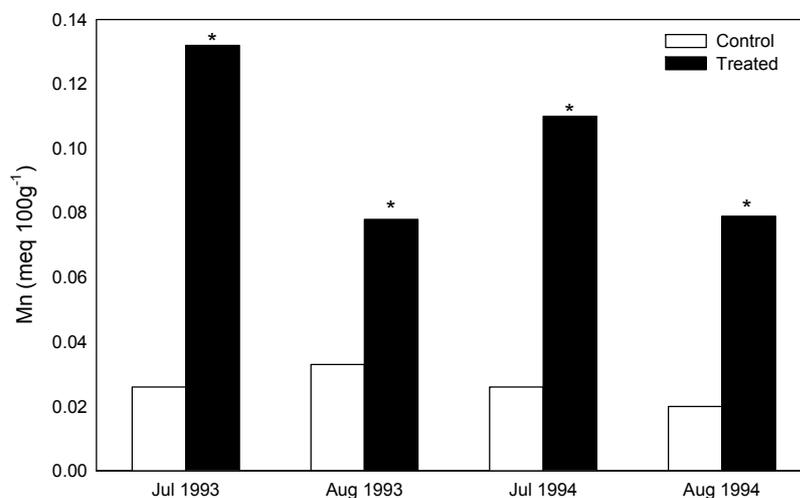


Figure 3-14. Mean SrCl<sub>2</sub> extractable Mn in the O horizon, WS9 (Pickens 1995). \* indicates statistically significant differences between treatments at  $\alpha < 0.05$ ;  $n = 6$ .

These results indicate significantly lower concentrations of Ca and Mg in the soil of the treatment plots relative to the control plots and also suggest that the availability of Al and Mn was increased significantly by the treatment. We hypothesize that base cation depletion of these soil horizons has occurred and Al and Mn availability have increased in response to the acidification treatment.

### 3.3.4 Soil N Cycling

A good deal of work has been dedicated to furthering our understanding of N cycling in the soil on these watersheds. When measuring nitrous oxide (N<sub>2</sub>O) production from WS3 and WS4, Peterjohn *et al.* (1998) reported that mean monthly rates of N<sub>2</sub>O production were consistent with measurements from other well-drained forest soils but much lower than those measured from N-rich sites with poorly drained soils. Chemoautotrophic nitrification accounted for 60% (WS3) and 40% (WS4) of total N<sub>2</sub>O production. Production of N<sub>2</sub>O on WS3 was constrained by low pH, while on WS4, it appeared that N<sub>2</sub>O production was constrained by low NO<sub>3</sub> availability, as evidenced by extremely low N<sub>2</sub>O production on south-facing slopes, where the lowest available NO<sub>3</sub> was found. The authors suggested this low NO<sub>3</sub> availability could be related to a distinct assemblage of woody vegetation (Christ *et al.* 2002). This low NO<sub>3</sub> availability on south-facing slopes of WS4 was also noted by Gilliam *et al.* (2001b) and is further evidence of high within-watershed spatial variability.

Venterea *et al.* (2004) measured nitric oxide (NO) emissions from plots on WS3 and WS7 in 2000-2001, and reported that on nearly every occasion that field measurements were made, mean NO emission rates were higher in plots within WS3, compared to those within WS7. Fluxes from the Fernow tended to be higher than those from Bear Brook Watersheds in Maine, but the differences were not significant. Field fluxes of NO were positively correlated with mineral soil NO<sub>3</sub> concentrations across all plots, suggesting that NO emissions may be a reliable indicator of NO<sub>3</sub> leaching potential. Decreased soil pH also provided evidence for the promotion of nitrification-derived NO production in Fernow soils.

Gilliam *et al.* (2001b) evaluated temporal and spatial variability in nitrogen transformations, particularly net mineralization and net nitrification on WS3 and WS4 and also on WS7. Net nitrification rates were high and were nearly 100% of net mineralization for all watersheds. Seasonal patterns of nitrification were related to soil moisture and ambient temperature in untreated watersheds. The spatial patterns in WS4 suggested that micro-environmental variability limits rates of N processing in some parts of this watershed. Spatial variability in soil N was lower in WS3, which the authors interpreted to mean that the N and S additions may have altered the responses

of N-processing microbes to environmental factors, becoming less sensitive to seasonal changes in soil moisture and temperature. Additional analyses by Gilliam et al. (2001a) suggested that the nitrifying bacteria were present on these low N processing plots, but herbaceous layer vegetation, particularly ericaceous vegetation, may have inhibited the nitrifier populations.

Williard et al. (1997) also found that net nitrification rates accounted for 100% of net mineralization rates on WS4, an indication that this untreated watershed had the potential for high NO<sub>3</sub> leaching. In that study, WS4 had the highest net mineralization and nitrification rates and NO<sub>3</sub> export of nine untreated forested watersheds in the mid-Appalachians. Net mineralization and nitrification rates served as strong indicators of NO<sub>3</sub> export from the nine study watersheds. High soil N cycling rates were related to high exchangeable Ca concentrations (an index to soil fertility), low soil C:N ratios, and high soil moisture (Williard et al. 1997). Christ et al. (2002) reported that net nitrification potentials on WS4 and WS10 were correlated with many soil characteristics related to base cation supply, C:N ratio and water holding capacity.

#### 4. DISCUSSION

The soil chemistry results from these watersheds provide interesting and apparently contradictory results. There are some indications of a direct soil response to the N and S additions on WS9 and WS3. For example, total N concentrations (WS3, WS9) and total S concentration (WS9) increased in the upper horizons of the soil, reflecting the elevated inputs of these two nutrients. There is also evidence that these changes have indirectly affected other processes including cycling of N, C and base cations. The increases in soil C may reflect a disruption of microbial activities. Tamm (1990) explained that the increase in N mineralization after application of high doses of acid in field experiments could depend on partial mortality of the microflora followed by mineralization of biomass N. Aber (1992, Aber et al. 1998) suggested that this was a short-term phenomenon, and that long-term increases in N mineralization were unlikely to occur, because a decrease in C mineralization following acidification should be accompanied by a corresponding decrease in net N mineralization. Persson et al. (1989) reported that, following acidification, a decrease in carbon dioxide (CO<sub>2</sub>) evolution was caused by lesser availability of C sources rather than a direct detrimental effect on the microorganisms. An 8% decrease in CO<sub>2</sub> evolution from WS3 relative to WS7 observed by Mattson and Adams (unpublished data, 1992) suggests some effect on C cycling. Increases in the organic matter in the O horizon during the study also support this hypothesis. Changes in

mineralization of N are often paralleled by changes in rates of net nitrification (Aber *et al.* 1998, Jefts *et al.* 2004). In this study, although we have seen no change in net N mineralization or nitrification rates, the continual additions of N may have led to an decoupling of the cycling of C and N. The acidification treatment also may have contributed to reduced decomposition rates; Adams and Angradi (1996) reported slower decomposition (mass loss) rates for leaf litter of some tree species from WS3 after 3 years of treatment, but without significant differences in nutrient loss rates.

There is some evidence to support the hypothesis that the treatment of WS3 and WS9 has accelerated base cation leaching and resulted in elevated concentrations of Al and Mn in the soil. The observed differences in mean soil properties between WS3 and WS7, for instance, are generally consistent with expectations of effects of acidification on soil properties. Exchangeable base cation concentrations, such as Ca and Mg, were lower on WS3 when compared to soil from WS7, as might be expected when excess acid anions are leached through the soil and carry base cations with them. The observed elevated Al concentrations in soil can also be expected as base cation concentrations and soil pH are reduced. On WS9, soil exchangeable Ca concentrations consistently were 1 to 2 times greater on the control plots than on the treatment plots. WS9 showed consistent differences in Ca concentrations between treated and control plots in 1993, 1994 and 1995. Mean A horizon pH on WS3 decreased slightly (from 4.48 in 1988 to 4.34 in 1994 and to 4.20 in 2002), providing further support for the hypothesis that the fertilizer treatment may be leading to soil acidification. Although we are unable to unequivocally attribute the changes that we detected to the acidification treatment, observations from various watersheds sampled at different points in time suggest common, perhaps expected, patterns of acidification effects.

However, effects were not always what we expected, nor did all data provide immediate support for our hypotheses. Although mean WS3 A horizon soil pH decreased between 1988 and 1994, mean A horizon soil pH on WS4 increased during this time period. We hypothesized decreases in soil base cation concentrations, particularly Ca and Mg, over time, although the time frame was uncertain. Such declines in mineral soil Ca and Mg levels have been documented in response to acidification elsewhere (Currie *et al.* 1999, Fernandez *et al.* 2003). However, mean mineral soil concentrations of Ca and Mg on WS3 were generally greater than on WS4, and where significant differences were detected, between 1994 and 2002 on WS3, they were *increases* in concentrations. Exchangeable Ca concentrations on WS3 in 2002 were nearly triple those observed in 1994, although a similar increase was also recorded for WS4 for the same time period. It is not likely to be a sampling artifact, e.g., due to mixing of more organic matter into the A horizon, as similar patterns were observed for the O horizon. Some of these

unexpected changes may be due in part to high spatial and temporal variability within the watershed—coefficients of variation for Ca concentration within a sampling horizon and year ranged from 50% to almost 200%. This apparent contradiction may also be a function of timing of sampling. Soil water Ca concentrations collected below the A horizon peaked in 1991 (see Chapter 4), decreased through 1996, then leveled off. Thus we might hypothesize that the levels of Ca in the A horizon in 1994 could represent an already depleted state, in which case, further change would not be expected. The increases between 1994 and 2002 do not fit well with this hypothesis, however. Finally, we may believe that the observed changes in organic matter are driving the chemistry of these upper horizons, and that the acidification treatment may have altered C and N relationships significantly.

Another unexpected observation was reported by Tepp (1995) for WS3 and WS7: soil Mn levels were lower on WS3 after 7 years of fertilizer treatment than on WS7. It was hypothesized that soil Mn would increase with acidification, as was observed for WS9. One explanation for the decrease on WS3 may be that exchangeable or plant available Mn levels in soil in the early stages of treatment may have been affected by two processes: cation mobilization and soil acidification. Manganese that occurred primarily as  $Mn^{2+}$  on soil exchange sites at the initiation of treatment could have been mobilized and leached, like base cations, causing exchangeable  $Mn^{2+}$  levels to initially diminish in the solid soil phase as observed in Tepp's soil samples. This could have produced a reduction in bolewood Mn as well. As base cations were depleted and soil began to acidify, Mn also could have been gradually mobilized, similar to soil Al, and then accumulated in bolewood tissue. Tepp's (1995) sampling could have occurred during the transition from Mn depletion due to cation leaching and Mn mobilization due to soil acidification. That some tree species showed such a transition from Mn depletion to Mn increase due to acidification between 4 and 8 years of treatment, provides some support for this explanation (see Chapter 5).

## 5. CONCLUSION

Analyses of soil samples from WS3, WS4, WS7, and WS9 provided some support for hypotheses of soil acidification as a result of the acidification treatment, and provided some results which do not appear to support our hypotheses. Generally, the greatest differences in soil chemistry of the treated and control watersheds were observed for the O horizon, suggesting that it is the most responsive to acidification treatment. However, there was considerable variability in response among watersheds, some of which may be due to spatial and temporal variability, and not all of the results support our hypotheses of base cation depletion. Further examination

of patterns of organic matter production and accumulation should be made. Changes in base cation cycling among the watersheds also may be difficult to detect, requiring more information than is available from soil sampling alone.

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