# The Fernow Watershed Acidification Study: Ecosystem Acidification, Nitrogen Saturation and Base Cation Leaching

Mary Beth Adams • James N. Kochenderfer • Pamela J. Edwards

Received: 13 June 2005 / Accepted: 3 April 2006 / Published online: 17 January 2007 © Springer Science + Business Media B.V. 2007

Abstract In 1989, a watershed acidification experiment was begun on the Fernow Experimental Forest in West Virginia, USA. Ammonium sulfate fertilizer  $(35.5 \text{ kg N ha}^{-1} \text{ yr}^{-1} \text{ and } 40.5 \text{ kg S ha}^{-1} \text{ yr}^{-1})$  was applied to a forested watershed (WS3) that supported a 20-year-old stand of eastern deciduous hardwoods. Additions of N and S are approximately twice the ambient deposition of nitrogen and sulfur in the adjacent mature forested watershed (WS4), that serves as the reference watershed for this study. Acidification of stream water and soil solution was documented, although the response was delayed, and acidification processes appeared to be driven by nitrate rather than sulfate. As a result of the acidification treatment. nitrate solution concentrations increased below all soil layers, whereas sulfate was retained by all soil layers after only a few years of the fertilization treatments, perhaps due to adsorption induced from decreasing sulfate deposition. Based on soil solution monitoring, depletion of calcium and magnesium was observed, first from the upper soil horizons and later from the lower soil horizons. Increased base cation concentrations in stream water also were documented and linked closely with high solution levels of nitrate.

P.O. Box 404, Parsons, WV 26287, USA e-mail: mbadams@fs.fed.us

Significant changes in soil chemical properties were not detected after 12 years of treatment, however.

Keywords acidic deposition  $\cdot$  base cation leaching  $\cdot$  forest soils  $\cdot$  nitrogen saturation  $\cdot$  soil solution chemistry

# **1** Introduction

In 1989, the Fernow Watershed Acidification Study began when experimental additions of ammonium sulfate first were made to a small forested watershed (WS3). An adjacent forested watershed (WS4) containing an older stand uncut since 1905, serves as a reference watershed for stream water and soil water chemistry. For vegetation comparisons, watershed 7 (WS7) is used because the stands began regrowth at the same time, in the spring of 1970 (Table 1). The original objective was to evaluate impacts of atmospheric deposition on stream water and soil leachate chemistry. Additional opportunistic research has addressed the effects of acidification on soil chemistry, amphibian populations, tree and stand growth, and nutrient cycling, among other topics. In this manuscript, we highlight some of the major biogeochemical findings from the Fernow Watershed Acidification Study, focusing on the processes of acidification, nitrogen (N) saturation, and base cation leaching.

M. B. Adams ( $\boxtimes$ )  $\cdot$  J. N. Kochenderfer  $\cdot$  P. J. Edwards USDA Forest Service,

Characteristic	WS3	WS4	WS7
Area (ha)	34	39	24
Aspect	South	Southeast	East
Stand age (yrs)	34	95	34
Mean stand density (stems $ha^{-1}$ )	1,883	1,206	1,473
Mean stand biomass (mt ha <sup>-1</sup> )	203.4	310.7	157.5
Dominant tree species (% basal area)	Black cherry (51.0)	Sugar maple (1.3)	Sugar maple (4.9)
	Red maple (11.5)	Red maple (8.9)	Sweet birch (20.5)
	American beech (2.5)	American beech (6.5)	Red maple (8.2)
	Sweet birch (5.1)	Northern red oak (29.8)	Yellow-poplar (26.2)
	Sugar maple (11.3)	Sweet birch (3.6)	Black cherry (20.5)

Table 1 Some characteristics of the study watersheds, Fernow Experimental Forest, West Virginia, USA

Stand parameters are based on the 1990 inventory for WS4, 2004 for WS3 and WS7.

# 2 Site Description

The Fernow Experimental Forest (FEF; 39.03°N, 79.67°W) is in north-central West Virginia, in the Allegheny Mountain section of the mixed mesophytic forest, within the central Appalachian Mountains. Prior to settlement, central Appalachian forests were shaped by disturbances such as wind, fire, and agricultural use, creating a diverse mosaic of forest stands. Recently, several insects and diseases, most of them non-native, have severely impacted Appalachian forests, and acidic deposition and other air pollutants represent a chronic disturbance (Adams, 1999).

Diversity is a hallmark of central Appalahcian forests, such as the FEF, and the vegetation fits into Core's (1966) mixed central hardwood forests floristic province. Madarish, Rodrigue, and Adams (2002) lists more than 500 species of vascular flora found on the FEF. Common tree species include yellow-poplar (*Liriodendron tulipifera* L.), sugar maple (*Acer saccharum* Marsh.), black cherry (*Prunus serotina* Ehrh.), northern red oak (*Quercus rubra* L.) red maple (*A. rubrum* L.), American beech (*Fagus grandifolia* Ehrh.), and sweet birch (*Betula lenta* L.), although their distribution is highly variable across the watersheds (Table 1).

The growing season on the FEF extends from May through October, and the average length of the frost free season is 145 days. Annual precipitation is about evenly distributed between growing and dormant seasons, averaging 145.8 cm. Precipitation often occurs in the form of snow during the winter but a snowpack usually does not exist for extended periods. Average annual air temperature is 9.2°C (Pan, Tajchman, & Kochenderfer, 1997), and mean monthly temperatures range from  $-18^{\circ}$ C in January to 20.6°C in July. Potential evapotranspiration on the Fernow was estimated to be 56 cm/year (Patric & Goswami, 1968).

The hydrometeorologic network of the Fernow is described by Adams, Kochenderfer, Wood, Angradi, and Edwards (1994). WS3, WS4, and WS7 are instrumented with 120° V-notch weirs, with FW-1 water level recorders and 7-day strip charts to measure streamflow continuously. Stream water grab samples have been collected from WS3, WS4, and WS7 on a weekly or bi-weekly basis since 1960. In addition to grab sampling, stream water also was sampled during storm runoff events using automatic pumping samplers. Zero-tension pan lysimeters were installed on WS3 and WS4 in 1988 to sample soil water for chemical analyses. Stream and soil water samples were analyzed at the USDA Forest Service Timber and Watershed Laboratory in Parsons, West Virginia, USA, using U.S. Environmental Protection Agency protocols (Edwards & Wood, 1993).

# 2.1 Watershed Acidification Treatment

Ammonium sulfate fertilizer was applied to WS3 at a rate that approximately doubled bulk deposition inputs of N and S estimated from throughfall concentrations (Helvey & Kunkle, 1986). Applications were made in spring, summer, and autumn (usually in March, July, and November) to reflect seasonal variability in deposition. Spring and autumn application rates were 34 kg fertilizer ha<sup>-1</sup> (7.1 kg N ha<sup>-1</sup> and 8.1 kg S ha<sup>-1</sup>), respectively. Summer application

rates were 101 kg fertilizer ha<sup>-1</sup> (21.3 kg N ha<sup>-1</sup> and 24.4 kg S ha<sup>-1</sup>). All applications on WS3 during the first 9 years were made by helicopter; beginning in July 1998 all applications to WS3 have been made by low flying fixed-wing aircraft equipped with a global positioning swathing system to ensure accurate coverage.

## **3** Results and Discussion

Application of ammonium sulfate fertilizer to WS3 during the Fernow Watershed Acidification Study has resulted in significant changes to several watershed parameters. Some of these effects were obvious and were consistent with published models of ecosystem acidification, N saturation and base cation cycling (Aber et al., 1998; Galloway, Norton, & Church, 1983; Norton, Fernandez, Kahl, & Reinhardt, 2003; Stoddard, 1994), while other effects were less so.

## 3.1 Acidification Processes

Fertilizer additions were effective in acidifying the ecosystem on WS3, based on stream and soil solution chemistry (Figs. 1 and 2). Additions of sulfate via the fertilizer treatment increased leaching of sulfate in stream water over time (Fig. 1). However, the sulfate response was not as rapid nor as substantial as we had hypothesized. Early in the experiment nitrate seemed to be a more important driver of changes in stream water chemistry. Sulfur retention by WS3 ranged from 72 to 91% of that applied (calculated from input-output budgets), and decreased slightly over time, but this decline was observed on most of the monitored watersheds on the FEF, not just WS3 (Adams, DeWalle, & Hom, 2006). Significant declines in ambient sulfate deposition during the course of the experiment (Lynch, Bowersox, & Grimm, 2000) could partially explain these results, as adsorption of sulfate is a partially reversible process and concentration-dependent (Reuss & Johnson, 1986).

Baseflow stream pH on WS3 decreased approximately 0.8 pH units, from around 6.0 to about 5.2, during the study (Fig. 1). Increased acidity on WS3 was statistically significant and resulted in WS3 baseflow moving from being only episodically acidic to chronically acidic based on stream pH and acid neutralizing capacity (ANC). A similar trend occurred for peakflow (Edwards, Williard, Wood, & Sharpe, 2006). Significant decreases in soil solution pH also indicate acidification (Fig. 2). However, soil chemical parameters were much less responsive to the treatments, and few significant differences in soil chemical parameters were detected between WS3 and WS4 soil chemistry, regardless of horizon sampled (Adams et al., 2006). This lack of treatment effect can be attributed at least partially to high spatial variability in soil chemistry within the watersheds (Adams et al., 2006; Gilliam, Yurish, & Adams, 2001; Peterjohn, Adams, & Gilliam, 1996). Also, soil solution chemistry may not mirror bulk soil chemistry, as the soil water collected in zero tension lysimeters reflects channelized or macropore flow.

#### 3.2 N Saturation

The fertilizer additions also affected N cycling on WS3, and may have induced N saturation (Aber et al., 1998; Peterjohn et al., 1996; Stoddard, 1994). The added N rapidly resulted in increased stream water nitrate concentrations (Fig. 1). Increased fluxes of nitric oxide (NO) gas also were detected (Venterea et al., 2004) in response to the treatment, along with decreased resorption of N prior to leaf senescence (May, Burdette, Gilliam, & Adams, 2005). Significant increases in foliar N concentrations on WS3 relative to WS7 were detected in 1992 for black cherry and red maple, but differences were not significant in 2002 foliage samples (DeWalle et al., 2006). These results provide some support for the idea of N saturation of the forest on WS3.

However, there was a significant positive growth response on WS3 plots dominated by black cherry and yellow poplar (Fig. 3). Biomass and volume growth on the treated WS3 exceeded that observed on WS7 for the 14 year measurement period, suggesting that N was limiting on WS3 for the entire measurement period, which appears to be inconsistent with models of N saturation (Aber et al., 1998; Stoddard, 1994). Other results also raise questions about the N status of these watersheds. For example, the Aber et al. (1998) model predicts that N mineralization will initially increase then decrease, while net nitrification increases. Yet despite additions of almost 500 kg ha<sup>-1</sup> of N to WS3 between 1989 and 2003, no significant differences in net N mineralization and nitrification Fig. 1 Flow-weighted mean monthly stream water concentrations of Ca, SO<sub>4</sub>, NO<sub>3</sub> and stream pH for WS3 (*solid line*) and WS4 (*dashed line*), Fernow Experimental Forest, West Virginia, USA. Vertical bar represents start of the ammonium sulfate fertilizer additions to WS3



rates could be detected between the watersheds, and rates were consistently high (Gilliam et al., 2001). Also, prior to initiation of the treatment, WS3 retained approximately 55% of N inputs from deposition (calculated from input–output budgets). Retention of the added fertilizer N was about 90% initially after fertilization treatments started (1990–1991), then declined to around 70% with continued N additions (2002). That N retention by a forest would increase after additions of more N is contrary to current understanding of N saturation.

Some of this lack of fit with N saturation conceptual models may be due to a greater resistance of hardwood/deciduous forests to N saturation relative Fig. 2 Volume-weighted mean concentrations for soil solution of Ca, Mg, K, SO<sub>4</sub>, NO<sub>3</sub> and pH by soil horizon from WS3 (*open squares*) and WS4 (*closed circles*), with *trend line overlaid*, Fernow Experimental Forest, West Virginia, USA. *Vertical bar* represents start of the ammonium sulfate fertilizer additions to WS3



to conifers. Larger pools of nutrients are cycled via annual litterfall in deciduous systems, resulting in different rates and processing of N. Research from Bear Brook Watershed in Maine (Fernandez, Rustad, Norton, Kahl, & Cosby, 2003) and elsewhere (Fenn et al., 1998) provides at least some support for the relatively greater sensitivity of conifer ecosystems to N saturation and acidification. Also, the timing of the fertilizer applications to WS3 may not be the most opportune for plant uptake and growth stimulation. In forest management applications, to maximize growth response, fertilizer would normally be applied around bud break in the spring. Much of the total N loading (43%) from both ambient deposition and the fertilizer treatment occurred in the 8-month period from September to May when vegetation was mostly dormant. About 80% of the nitrate was exported in stream water from the fertilized watershed between December and May. Thus, the question arises whether WS3 is saturated with N throughout the year, or is responding to chronic N deposition and artificial N inputs by leaching N during periods that do not coincide with high biotic demands. Clearly, there is a need for an improved understanding, both temporally and spatially, of N dynamics and N saturation in temperate deciduous forest ecosystems.

### 3.3 Base Cation Leaching

Evidence exists that the fertilization treatment has affected the cycling of base cations, particularly calcium (Ca), within WS3. Soil solution concentrations of Ca and magnesium (Mg) increased during the early years of treatment, and then decreased in the later years of the study (Fig. 2). This pattern of base cation increases and decreases also was evident in stream water during peakflow, but was less obvious in stream water concentrations at baseflow (Edwards et al., 2006), although significant increases in stream water baseflow concentrations and exports of base cations were observed during the first few years of treatment (Fig. 1), consistent with acidification models (Fernandez et al., 2003; Galloway et al., 1983; Norton & Fernandez, 1999; Norton et al., 2003). This pattern can be interpreted as a cycle of



**Fig. 3** Mean net annual (1990–2004) biomass production by trees on growth plots, WS3 (*open bars*) and WS7 (*dark bars*), Fernow Experimental Forest, West Virginia, USA. Plots were stratified by a higher occurrence of *black cherry/yellow-poplar* (BC/YP) or *red maple/sweet birch* (RM/SB). Numbers *above* means are significance levels, indicating probability > F statistic for each comparison



Fig. 4 Relative radial growth patterns for 10 *black cherry trees* on WS3 (*dashed line*) and WS7 (*solid line*), Fernow Experimental Forest, West Virginia, USA, during acidification treatments which began in 1989. *Asterisks by year* indicate significant differences;  $*\alpha=0.1$ ,  $**\alpha=0.05$ . (From DeWalle et al., 2006)

increasing base cation mobility, followed by depletion of available base cations from the soil exchange sites as hypothesized by Norton et al. (2003). Patterns of tree ring chemistry and radial growth of some tree species are approximately concurrent with the trends of mobilization and depletion observed in the soil water chemistry (Fig. 4). However, no significant decreases in soil base cation concentrations or soil base saturation were detected. Nor were any obvious signs of tree decline (crown dieback, mortality.) observed.

### **4** Conclusions

During the first 15 years of the Fernow Watershed Acidification Study, much has been learned; the processes of acidification, N saturation and base cation leaching have been documented as a result of the treatments. As treatment of WS3 has continued, we have found that some conceptual models have been useful in predicting responses, while others do not seem to "fit" the deciduous hardwood forest ecosystem of WS3. The central hardwood forest type is one of the most widespread in the United States (Adams, Burger, Jenkins, & Zelany, 2000), and therefore we need to better understand the effects of atmospheric deposition on these important forest ecosystems. Continuation of the Fernow Watershed Acidification Study will help address this need. Acknowledgements This experiment was planned and conducted largely by personnel of the USDA Forest Service, Northeastern Research Station at Parsons, West Virginia, USA, with initial funding from the US Environmental Protection Agency. Subsequent support by the USDA Forest Service Northern Global Change Program, and the National Science Foundation's Long-term Research in Environmental Biology Program are also acknowledged.

#### References

- Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., et al. (1998). Nitrogen saturation in temperate forest ecosystems: Hypotheses revisited. *Biosci*ence, 48, 921–934.
- Adams, M. B. (1999). Acidic deposition and sustainable forest management in the central Appalachians, USA. Forest Ecology and Management, 122, 17–28.
- Adams, M. B., Burger, J. A., Jenkins, A. B., & Zelazny, L. (2000). Impact of harvesting and atmospheric pollution on nutrient depletion of eastern US hardwood forests. *Forest Ecology and Management*, 138, 301–319.
- Adams, M. B., DeWalle, D. R., & Hom, J. (Eds.) (2006). The Fernow watershed acidification study (p. 290). Berlin Heidelberg New York: Springer.
- Adams, M. B., Kochenderfer, J. N., Wood, F., Angradi, T. R., & Edwards, P. J. (1994). Forty years of hydrometeorological data on the Fernow Experimental Forest, West Virginia. USDA Forest Service General Technical Report NE-184. Radnor, PA. 24 p.
- Core, E. L. (1966). Vegetation of West Virginia (p. 217). Parsons, WV: McClain.
- DeWalle, D. R., Kochenderfer, J. N., Adams, M. B., Miller, G. W., Gilliam, F. S., Wood, F., et al. (2006). Vegetation and acidification. In M. B. Adams, D. R. DeWalle, & J. Hom (Eds.), *The Fernow watershed acidification study* (pp. 137–188). Berlin Heidelberg New York: Springer.
- Edwards, P. J., Williard, K. W. J., Wood, F., & Sharpe, W. E. (2006). Soil water and stream water chemical responses. In M. B. Adams, D. R. DeWalle, & J. Hom (Eds.), *The Fernow watershed acidification study* (pp. 71–136). Berlin Heidelberg New York: Springer.
- Edwards, P. J., & Wood, F. (1993). Fernow experimental forest watershed acidification project: Field and laboratory quality assurance/quality control protocols. USDA Forest Service General Technical Report NE-177. Radnor, PA 15 p.
- Fenn, M. E., Poth, M. A., Aber, J. D., Baron, J. S., Bormann, B. T., Johnson, D. W., et al. (1998). Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. *Ecological Applications*, 8, 706–733.
- Fernandez, I. J., Rustad, L. E., Norton, S. A., Kahl, J. S., & Cosby, B. J. (2003). Experimental acidification causes soil base-cation depletion at the Bear Brook Watershed in Maine. *Soil Science Society of America Journal*, 67, 1909– 1919.

- Galloway, J. N., Norton, S. A., & Church, M. R. (1983). Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model. *Environmental Science* & Technology, 17, 541A–545A.
- Gilliam, F. S., Yurish, B. M., & Adams, M. B. (2001). Temporal and spatial variation of nitrogen transformations in nitrogen saturated soils of a central Appalachian hardwood forest. *Canadian Journal of Forest Research*, 31, 1768–1785.
- Helvey, J. D., & Kunkle, S. H. (1986). Input–output budgets of selected nutrients on an experimental watershed near Parsons, West Virginia. USDA Forest Service General Technical Report NE-584. Broomall, PA. 7 p.
- Lynch, J. A., Bowersox, V. C., & Grimm, J. W. (2000). Changes in sulfate deposition in eastern USA following implementation of phase I of Title IV of the Clean Air Act Amendments of 1990. *Atmospheric Environment*, 34(11), 1665–1680.
- Madarish, D. M., Rodrigue, J. L., & Adams, M. B. (2002). Vascular flora and macroscopic fauna on the Fernow Experimental Forest, USDA Forest Service. General Technical Report NE-291. Newtown Square, PA. 37 p.
- May, J. D., Burdette, S. B., Gilliam, F. S., & Adams, M. B. (2005). Interspecific divergence in foliar nutrient dynamics and stem growth in response to excessive nitrogen deposition in a temperate forest. *Forest Ecology and Management*, 35, 1023–1030.
- Norton, S. A., & Fernandez, I. J. (Eds.) (1999). The Bear Brook Watershed in Maine: A paired watershed experiment – The first decade (1987–1997). Boston, MA: Kluwer.
- Norton, S. A., Fernandez, I. J., Kahl, J. S., & Reinhardt, R. L. (2003). Acidification trends and the evolution of neutralization mechanisms through time at the Bear Brook Watershed in Maine (BBWM). *Water, Air, & Soil Pollution. Focus, 4*, 289–310.
- Pan, C., Tajchman, S. J., & Kochenderfer, J. N. (1997). Dendroclimatological analysis of major forest species of the central Appalachians. *Forest Ecology and Management*, 98, 77–87.
- Patric, J. H., & Goswami, N. (1968). Evaporation pan studies Forest research at Parsons. West Virginia Agriculture and Forestry, 1(4), 6–10.
- Peterjohn, W. T., Adams, M. B., & Gilliam, F. S. (1996). Symptoms of nitrogen saturation in two central Appalachian hardwood forest ecosystems. *Biogeochemistry*, 35, 507–522.
- Reuss, J. O., & Johnson, D. W. (1986). Acid deposition and the acidification of soils and waters (p. 119). Berlin Heidelberg New York: Springer.
- Stoddard, J. L. (1994). Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. In L. A. Baker (Ed.), *Environmental chemistry of lakes and reservoirs. Advances in chemistry series, vol.* 237 (pp. 223–284). Washington, DC: American Chemical Society.
- Venterea, R. T., Groffman, P. M., Castro, M. S., Verchot, L. V., Fernandez, I. J., & Adams, M. B. (2004). Soil emission of nitric oxide in two forest watershed subjected to elevated N inputs. *Forest Ecology and Management*, 196, 335–349.